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Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industry Background Information for Proposed Standards

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

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Standards of Performance for the control of emissions from air oxidation processes in the synthetic organic chemical manufacturing industry are being proposed under the authority of Section 111 of the Clean Air Act. These standards would apply to new, modified, and reconstructed air oxidation facilities. This document contains background information and environmental and economic impact assessments of the regulatory alternatives considered in developing proposed standards.

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Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industry — Background Information for Proposed Standards

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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ENVIRONMENTAL PROTECTION AGENCY

Background Information
and Draft
Environmental Impact Statement
for SOCMI Air Oxidation Unit Processes

Prepared by:

Don R Goodwin 12/23/82

Don R. Goodwin (Date)
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1. The proposed standards of performance would limit emissions of volatile organic compounds from new, modified, and reconstructed SOCMI air oxidation process. Section 111 of the Clean Air Act (42 U.S.C. 7411), as amended, directs the Administrator to establish standards of performance for any category of new stationary source of air pollution that ". . . causes or contributes significantly to air pollution which may reasonably be anticipated to endanger public health or welfare." The Gulf Coast and Northeast regions would be particularly affected by the proposed standards.

2. Copies of this document have been sent to the following Federal Departments: Labor, Health and Human Services, Defense, Transportation, Agriculture, Commerce, Interior, and Energy; The National Science Foundation; the Council on Environmental Quality; members of the State and Territorial Air Pollution Program Administrators; the Association of Local Air Pollution Control Officials; EPA Regional Administrators; and other interested parties.

3. The comment period for review of this document is 60 days. Ms. Susan R. Wyatt may be contacted regarding the date of the comment period.

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1. SUMMARY

Background information on proposed new source performance standards for the Synthetic Organic Chemical Manufacturing Industry (SOCMI) air oxidation processes is contained in this document. New source performance standards are proposed under authority of Section 111, 301(a) of the Clean Air Act, as amended.

1.1 REGULATORY ALTERNATIVES

The regulatory alternatives are based upon a single VOC control technique, thermal oxidation, which is the most effective control technology and is demonstrated for application at all facilities. All new thermal oxidizers can achieve at least a 98 weight percent VOC reduction, or VOC reduction to 20 ppmv (by compound). Accordingly, each alternative would require this degree of VOC emission reduction for those affected facilities required to reduce emissions. Under each successive regulatory alternative, an additional percentage of projected affected facilities would be subjected to the standards. Each successive increment of sources required to meet the standards would have a higher per unit control cost than the increment of sources added under the previous alternative.

Alternative 0 represents the baseline level of control. Under Alternatives I through VI, the percentages of all projected facilities covered by the air oxidation NSPS would be 7, 14, 19, 27, 47, and 100, respectively.

A maximum or cutoff value of total resource effectiveness (TRE) is associated with each regulatory alternative. The TRE value of a facility is proportional to the cost of incineration, per megagram of VOC destroyed, for that facility. The TRE value of a facility is an algebraic function of the vent stream flowrate, heating value, VOC emission rate, and corrosion properties (presence of chlorinated compounds). A facility with a TRE value below the cutoff TRE value associated with a given alternative would be required to reduce VOC emissions by 98 percent or to 20 ppmv under that alternative. However, the regulatory alternatives are structured to allow such a facility to add a product recovery device or improve an existing product recovery device to change the vent stream characteristics used for calculating the TRE value. As a result of this change, the TRE value for such a facility would be increased beyond the cutoff value associated with the given alternative and incineration would not be required. Such increased product recovery would have the advantages over incineration of lower cost and less energy usage.

1.2 ENVIRONMENTAL IMPACT

The environmental impacts of the regulatory alternatives have been analyzed. A matrix of environmental and economic impacts for each regulatory alternative considered is given in Table 1-1. As indicated in Section 1.1, each alternative is based upon a single VOC control technqiue, thermal oxidation, which is universally applicable to air oxidation processes.

Under Alternative I, projected 1986 national VOC emissions from new, modified, or reconstructed air oxidation facilities would be reduced by an estimated 6,600 Mg/yr. This national VOC reduction would be approximately 31 percent beyond the 22,000 Mg/yr level that would be expected under typical State implementation plans (SIP's).

Under Alternative II, projected 1986 national VOC emissions would be reduced by an estimted 10,000 Mg/yr. This represents a reduction of about 46 percent from the projected baseline emissions level.

Under Alternative III, projected 1986 national VOC emissions would be reduced by an estimated 12,500 Mg/yr. This represents a reduction of about 57 percent from the projected baseline emissions level.

Under Alternative IV, projected 1986 national VOC emissions would be reduced by an estimated 14,000 Mg/yr. This represents a reduction of about 66 percent from the projected baseline emissions level.

Under Alternative V, projected 1986 national VOC emissions would be reduced by an estimated 17,500 Mg/yr. This represents a reduction of about 81 percent from the projected baseline emissions level.

Under Alternative VI, projected 1986 national VOC emissions would be reduced by an estimated 21,000 Mg/yr. This represents a reduction of 98 percent from the projected baseline emissions level.

Any increase in emissions of other air pollutants as a result of controlling VOC emissions would be negligible. There would be no direct solid waste impacts under any of the regulatory alternatives, and impacts on noise, space requirements, and availability of resources would be negligible.

TABLE 1-1. MATRIX OF ENVIRONMENTAL AND ECONOMIC IMPACTS FOR EACH REGULATORY ALTERNATIVE CONSIDERED

Administrative Action	Air Impact	Water Impact	Solid Waste Impact	Energy Impact	Economic Impact
Regulatory Alternative 0 (Baseline)	0	0	0	0	0
Regulatory Alternative I	+3	0	0	-1	-1
Regulatory Alternative II	+3	0	0	-1	-1
Regulatory Alternative III	+4	0	0	-1	-1
Regulatory Alternative IV	+4	-1	0	-1	-1
Regulatory Alternative V	+4	-1	0	-2	-1
Regulatory Alternative VI	+4	-1	0	-2	-1

KEY:
0 No Impact
1 Negligible Impact
2 Small Impact
3 Moderate Impact
4 Large Impact
+ Beneficial Impact
- Adverse Impact

No increase in total plant wastewater is projected under Alternatives I, II, or III. There is no organic wastewater effluent associated with incineration. Therefore, the only facilities which could have an associated water pollution impact are those which might use additional product recovery to raise a total resource-effectiveness (TRE) value. Carbon adsorption is the only product recovery technique currently in use in the industry which has an associated organic wastewater effluent. Based on past industry experience, very few new air oxidation facilities are expected to employ carbon adsorption. Therefore, the wastewater generated under the first three alternatives is expected to be minimal. The few air oxidation facilities which might employ additional carbon adsorption are projected to be covered only under Alternatives IV, V, and/or VI. Therefore, under these alternatives, a small water pollution impact might result.

The projected fifth year energy use under Alternative I would be 230 million MJ/yr (110 bbl oil/day). The projected fifth year energy use under Alternative II would be 520 million MJ/yr (240 bbl oil/day). The projected fifth year energy use under Alternative III would be 770 million MJ/yr (360 bbl oil/day). The projected fifth year energy use under Alternative IV would be 1.0 billion MJ/yr (460 bbl oil/day). The projected fifth year energy use under Alternative V would be 2.4 billion MJ/yr (1,100 bbl oil/day). The projected fifth year energy use under Alternative VI would be 6.0 billion MJ/yr (2,800 bbl oil/day).

1.3 ECONOMIC IMPACT

The projected total fifth year capital cost to the air oxidation industry under Alternative I would be $6.1 million. The projected total fifth-year annualized cost to the industry under this alternative would be $3.0 million/yr.

The projected fifth-year national capital cost under Alternative II would be $13 million. The projected fifth-year annualized cost under this alternative would be $7.0 million/yr.

The projected fifth-year national capital cost under Alternative III would be $18 million. The projected fifth-year annualized cost under this alternative would be $10 million/yr.

The projected fifth-year national capital cost under Alternative IV would be $26 million. The projected fifth-year annualized cost under this alternative would be $15 million/yr.

The projected fifth-year national capital cost under Alternative V would be $42 million. The projected fifth-year annualized cost under this alternative would be $28 million/yr.

The projected fifth-year national capital cost under Alternative VI would be $87 million. The projected fifth-year annualized cost under this alternative would be $67 million/yr.

The projected capital and annualized costs under each alternative were judged to be reasonable. An economic analysis indicated that the costs of VOC control due to each alternative could be passed on with a negligible effect on the profitability of the air oxidation industry. The projected price changes for air oxidation chemicals expected to have new facilities in the fifth year, assuming that costs of 98 percent VOC reduction would be passed through totally, would range from zero to a 3.1 percent increase.

2. INTRODUCTION

2.1 BACKGROUND AND AUTHORITY FOR STANDARDS

Before standards of performance are proposed as a Federal regulation, air pollution control methods available to the affected industry and the associated costs of installing and maintaining the control equipment are examined in detail. Various levels of control based on different technologies and degrees of efficiency are expressed as regulatory alternatives. Each of these alternatives is studied by EPA as a prospective basis for a standard. The alternatives are investigated in terms of their impacts on the economics and well-being of the industry, the impacts on the national economy, and the impacts on the environment. This document summarizes the information obtained through these studies so that interested persons will be able to see the information considered by EPA in the development of the proposed standard.

Standards of performance for new stationary sources are established under section 111 of the Clean Air Act (42 U.S.C. 7411) as amended, hereinafter referred to as the Act. Section 111 directs the Administrator to establish standards of performance for any category of new stationary source of air pollution which ". . . causes, or contributes significantly to air pollution which may reasonably be anticipated to endanger public health or welfare."

The Act requires that standards of performance for stationary sources reflect ". . . the degree of emission reduction achievable which (taking into consideration the cost of achieving such emission reduction, and any nonair quality health and environmental impact and energy requirements) the Administrator determines has been adequately demonstrated for that category of sources." The standards apply only to stationary sources, the construction or modification of which commences after regulations are proposed by publication in the Federal Register.

The 1977 amendments to the Act altered or added numerous provisions that apply to the process of establishing standards of performance.

1. EPA is required to list the categories of major stationary sources that have not already been listed and regulated under standards of performance. Regulations must be promulgated for these new categories on the following schedule:

a. 25 percent of the listed categories by August 7, 1980.
b. 75 percent of the listed categories by August 7, 1981.
c. 100 percent of the listed categories by August 7, 1982.

A governor of a State may apply to the Administrator to add a category not on the list or may apply to the Administrator to have a standard of performance revised.

2. EPA is required to review the standards of performance every four years and, if appropriate, revise them.

3. EPA is authorized to promulgate a standard based on design, equipment, work practice, or operational procedures when a standard based on emission levels is not feasible.

4. The term "standards of performance" is redefined, and a new term "technological system of continuous emission reduction" is defined. The new definitions clarify that the control system must be continuous and may include a low- or non-polluting process or operation.

5. The time between the proposal and promulgation of a standard under section 111 of the Act may be extended to six months.

Standards of performance, by themselves, do not guarantee protection of health or welfare because they are not designed to achieve any specific air quality levels. Rather, they are designed to reflect the degree of emission limitation achievable through application of the best adequately demonstrated technological system of continuous emission reduction, taking into consideration the cost of achieving such emission reduction, any non-air-quality health and environmental impacts, and energy requirements.

Congress had several reasons for including these requirements. First, standards with a degree of uniformity are needed to avoid situations where some States may attract industries by relaxing standards relative to other States. Second, stringent standards enhance the potential for long-term growth. Third, stringent standards may help achieve long-term cost savings by avoiding the need for more expensive retrofitting when pollution ceilings may be reduced in the future. Fourth, certain types of standards for coalburning sources can adversely affect the coal market by driving up the price of low-sulfur coal or effectively excluding certain coals from the reserve base because their untreated pollution potentials are high. Congress does not intend that new source performance standards contribute to these problems. Fifth, the standard-setting process should create incentives for improved technology.

Promulgation of standards of performance does not prevent State or local agencies from adopting more stringent emission limitations for the same sources. States are free under section 116 of the Act to establish even more stringent emission limits than those established under section 111 or those necessary to attain or maintain the National Ambient Air Quality Standards (NAAQS) under section 110. Thus, new sources may in some cases be subject to limitations more stringent than standards of performance under section 111, and prospective owners and operators of new sources should be aware of this possibility in planning for such facilities.

A similar situation may arise when a major emitting facility is to be constructed in a geographic area that falls under the prevention of significant deterioration of air quality provisions of Part C of the Act. These provisions require, among other things, that major emitting facilities to be constructed in such areas are to be subject to best available control technology. The term Best Available Control Technology (BACT), as defined in the Act, means

> . . . an emission limitation based on the maximum degree of reduction of each pollutant subject to regulation under this Act emitted from, or which results from, any major emitting facility, which the permitting authority, on a case-by-case basis, taking into account energy, environmental, and economic impacts and other costs, determines is achievable for such facility through application of production processes and available methods, systems, and techniques, including fuel cleaning or treatment or innovative fuel combustion techniques for control of each such pollutant. In no event shall application of "best available control technology" result in emissions of any pollutants which will exceed the emissions allowed by any applicable standard established pursuant to sections 111 or 112 of this Act. (Section 169(3))

Although standards of performance are normally structured in terms of numerical emission limits where feasible, alternative approaches are sometimes necessary. In some cases physical measurement of emissions from a new source may be impractical or exorbitantly expensive. Section 111(h) provides that the Administrator may promulgate a design or equipment standard in those cases where it is not feasible to prescribe or enforce a standard of performance. For example, emissions of hydrocarbons from storage vessels for petroleum liquids are greatest during tank filling. The nature of the emissions, high concentrations for short periods during filling and low concentrations for longer periods during storage, and the configuration of storage tanks make direct emission measurement impractical. Therefore, a more practical approach to standards of performance for storage vessels has been equipment specification.

In addition, section 111(i) authorizes the Administrator to grant waivers of compliance to permit a source to use innovative continuous emission control technology. In order to grant the waiver, the Administrator must find: (1) a substantial likelihood that the technology will produce greater emission reductions than the standards require or an equivalent reduction at lower economic energy or environmental cost; (2) the proposed system has not been adequately demonstrated; (3) the technology will not cause or contribute to an unreasonable risk to the public health, welfare, or safety; (4) the governor of the State where the source is located consents; and (5) the waiver will not prevent the attainment or maintenance of any ambient standard. A waiver may have conditions attached to assure the source will not prevent attainment of any NAAQS. Any such condition will have the force of a performance standard. Finally, waivers have definite end dates and may be terminated earlier if the conditions are not met or if the system fails to perform as expected. In such a case, the source may be given up to 3 years to meet the standards with a mandatory progress schedule.

2.2 SELECTION OF CATEGORIES OF STATIONARY SOURCES

Section 111 of the Act directs the Adminstrator to list categories of stationary sources. The Administrator ". . . shall include a category of sources in such list if in his judgment it causes, or contributes significantly to, air pollution which may reasonably be anticipated to endanger public health or welfare." Proposal and promulgation of standards of performance are to follow.

Since passage of the Clean Air Amendments of 1970, considerable attention has been given to the development of a system for assigning priorities to various source categories. The approach specifies areas of interest by considering the broad strategy of the Agency for implementing the Clean Air Act. Often, these "areas" are actually pollutants emitted by stationary sources. Source categories that emit these pollutants are evaluated and ranked by a process involving such factors as (1) the level of emission control (if any) already required by State regulations, (2) estimated levels of control that might be required from standards of performance for the source category, (3) projections of growth and replacement of existing facilities for the source category, and (4) the estimated incremental amount of air pollution that could be prevented in a preselected future year by standards of performance for the source category. Sources for which new source performance standards were promulgated or under development during 1977, or earlier, were selected on these criteria.

The Act amendments of August 1977 establish specific criteria to be used in determining priorities for all major source categories not yet listed by EPA. These are (1) the quantity of air pollutant emissions that each such category will emit, or will be designed to emit; (2) the extent to which each such pollutant may reasonably be anticipated to endanger public health or welfare; and (3) the mobility and competitive nature of each such category of sources and the consequent need for nationally applicable new source standards of performance.

The Administrator is to promulgate standards for these categories according to the schedule referred to earlier.

In some cases it may not be feasible immediately to develop a standard for a source category with a high priority. This might happen when a program of research is needed to develop control techniques or because techniques for sampling and measuring emissions may require refinement. In the developing of standards, differences in the time required to complete the necessary investigation for different source categories must also be considered. For example, substantially more time may be necessary if numerous pollutants must be investigated from a single source category. Further, even late in the development process the schedule for completion of a standard may change. For example, inablility to obtain emission data from well-controlled sources in time to pursue the development process in a systematic fashion may force a change in scheduling. Nevertheless, priority ranking is, and will continue to be, used to establish the order in which projects are initiated and resources assigned.

After the source category has been chosen, the types of facilities within the source category to which the standard will apply must be determined. A source category may have several facilities that cause air pollution, and emissions from some of these facilities may vary from insignificant to very expensive to control. Economic studies of the source category and of applicable control technology may show that air pollution control is better served by applying standards to the more severe pollution sources. For this reason, and because there is no adequately demonstrated system for controlling emissions from certain facilities, standards often do not apply to all facilities at a source. For the same reasons, the standards may not apply to all air pollutants emitted. Thus, although a source category may be selected to be covered by a standard of performance, not all pollutants or facilities within that source category may be covered by the standards.

2.3 PROCEDURE FOR DEVELOPMENT OF STANDARDS OF PERFORMANCE

Standards of performance must (1) realistically reflect best demonstrated control practice; (2) adequately consider the cost, the non-air-quality health and environmental impacts, and the energy requirements of such control; (3) be applicable to existing sources that are modified or reconstructed as well as new installations; and (4) meet these conditions for all variations of operating conditions being considered anywhere in the country.

The objective of a program for developing standards is to identify the best technological system of continuous emission reduction that has been adequately demonstrated. The standard-setting process involves three principal phases of activity: (1) information gathering, (2) analysis of the information, and (3) development of the standard of performance.

During the information-gathering phase, industries are queried through a telephone survey, letters of inquiry, and plant visits by EPA representatives. Information is also gathered from many other sources, and a literature search is conducted. From the knowledge acquired about the industry, EPA selects certain plants at which emission tests are conducted to provide reliable data that characterize the pollutant emissions from well-controlled existing facilities.

In the second phase of a project, the information about the industry and the pollutants emitted is used in analytical studies. Hypothetical "model plants" are defined to provide a common basis for analysis. The model plant definitions, national pollutant emission data, and existing State regulations governing emissions from the source category are then used in establishing "regulatory alternatives." These regulatory alternatives are essentially different levels of emission control.

EPA conducts studies to determine the impact of each regulatory alternative on the economics of the industry and on the national economy, on the environment, and on energy consumption. From several possibly applicable alternatives, EPA selects the single most plausible regulatory alternative as the basis for a standard of performance for the source category under study.

In the third phase of a project, the selected regulatory alternative is translated into a standard of performance, which, in turn, is written in the form of a Federal regulation. The Federal regulation, when applied to newly constructed plants, will limit emissions to the levels indicated in the selected regulatory alternative.

As early as is practical in each standard-setting project, EPA representatives discuss the possibilities of a standard and the form it might take with members of the National Air Pollution Control Techniques Advisory Committee. Industry representatives and other interested parties also participate in these meetings.

The information acquired in the project is summarized in the Background Information Document (BID). The BID, the standard, and a preamble explaining the standard are widely circulated to the industry being considered for control, environmental groups, other government agencies, and offices within EPA. Through this extensive review process, the points of view of expert reviewers are taken into consideration as changes are made to the documentation.

A "proposal package" is assembled and sent through the offices of EPA Assistant Administrators for concurrence before the proposed standard is officially endorsed by the EPA Administrator. After being approved by the EPA Administrator, the preamble and the proposed regulation are published in the Federal Register.

As a part of the Federal Register announcement of the proposed regulation, the public is invited to participate in the standard-setting process. EPA invites written comments on the proposal and also holds a public hearing to discuss the proposed standard with interested parties. All public comments are summarized and incorporated into a second volume of the BID. All information reviewed and generated in studies in support of the standard of performance is available to the public in a "docket" on file in Washington, D.C.

Comments from the public are evaluated, and the standard of performance may be altered in response to the comments.

The significant comments and EPA's position on the issues raised are included in the "preamble" of a promulgation package," which also contains the draft of the final regulation. The regulation is then subjected to another round of review and refinement until it is approved by the EPA Administrator. After the Administrator signs the regulation, it is published as a "final rule" in the Federal Register.

2.4 CONSIDERATION OF COSTS

Section 317 of the Act requires an economic impact assessment with respect to any standard of performance established under Section 111 of the Act. The assessment is required to contain an analysis of: (1) the costs of compliance with the regulation, including the extent to which the cost of compliance varies depending on the effective date of the regulation and the development of less expensive or more efficient methods of compliance; (2) the potential inflationary or recessionary effects of the regulation; (3) the effects the regulation might have on small business with respect to competition; (4) the effects of the regulation on consumer costs; and (5) the effects of the regulation on energy use. Section 317 also requires that the economic impact assessment be as extensive as practicable.

The economic impact of a proposed standard upon an industry is usually addressed both in absolute terms and in terms of the control costs that would be incurred as a result of compliance with typical, existing State control regulations. An incremental approach is necessary because both new and existing plants would be required to comply with State regulations in the absence of a Federal standard of performance. This approach requires a detailed analysis of the economic impact from the cost differential that would exist between a proposed standard of performance and the typical State standard.

Air pollutant emissions may cause water pollution problems, and captured potential air pollutants may pose a solid waste disposal problem. The total environmental impact of an emission source must, therefore, be analyzed and the costs determined whenever possible.

A thorough study of the profitability and price-setting mechanisms of the industry is essential to the analysis so that an accurate estimate of potential adverse economic impacts can be made for proposed standards. It is also essential to know the capital requirements for pollution control systems already placed on plants so that the additional capital requirements necessitated by these Federal standards can be placed in proper perspective. Finally, it is necessary to assess the availability of capital to provide the additional control equipment needed to meet the standards of performance.

2.5 CONSIDERATION OF ENVIRONMENTAL IMPACTS

Section 102(2)(C) of the National Environmental Policy Act (NEPA) of 1969 requires Federal agencies to prepare detailed environmental impact statements on proposals for legislation and other major Federal actions significantly affecting the quality of the human environment. The objective of NEPA is to build into the decisionmaking process of Federal agencies a careful consideration of all environmental aspects of proposed actions.

In a number of legal challenges to standards of performance for various industries, the United States Court of Appeals for the District of Columbia Circuit has held that environmental impact statements need not be prepared by the Agency for proposed actions under section 111 of the Clean Air Act. Essentially, the Court of Appeals has determined that the best system of emission reduction requires the Administrator to take into account counter-productive environmental effects of a proposed standard, as well as economic costs to the industry. On this basis, therefore, the Court established a narrow exemption from NEPA for EPA determination under section 111.

In addition to these judicial determinations, the Energy Supply and Environmental Coordination Act (ESECA) of 1974 (PL-93-319) specifically exempted proposed actions under the Clean Air Act from NEPA requirements. According to section 7(c)(1), "No action taken under the Clean Air Act shall be deemed a major Federal action significantly affecting the quality of the human environment within the meaning of the National Environmental Policy Act of 1969." (15 U.S.C. 793(c)(1))

Nevertheless, the Agency has concluded that the preparation of environmental impact statements could have beneficial effects on certain regulatory actions. Consequently, although not legally required to do so by section 102(2)(C) of NEPA, EPA has adopted a policy requiring that environmental impact statements be prepared for various regulatory actions, including standards of performance developed under section 111 of the Act. This voluntary preparation of environmental impact statements, however, in no way legally subjects the Agency to NEPA requirements.

To implement this policy, a separate section in this document is devoted solely to an analysis of the potential environmental impacts associated with the proposed standards. Both adverse and beneficial impacts in such areas as air and water pollution, increased solid waste disposal, and increased energy consumption are discussed.

2.6 IMPACT ON EXISTING SOURCES

Section 111 of the Act defines a new source as ". . . any stationary source, the construction or modification of which is commenced . . ." after the proposed standards are published. An existing source is redefined as a new source if "modified" or "reconstructed" as defined in amendments to the general provisions of Subpart A of 40 CFR Part 60, which were promulgated in the Federal Register on December 16, 1975 (40 FR 58416).

Promulgation of a standard of performance requires States to establish standards of performance for existing sources in the same industry under section 111 (d) of the Act if the standard for new sources limits emissions of a designated pollutant (i.e., a pollutant for which air quality criteria have not been issued under section 108 or which has not been listed as a hazardous pollutant under section 112). If a State does not act, EPA must establish such standards. General provisions outlining procedures for control of existing sources under section 111(d) were promulgated on November 17, 1975, as Subpart B of 40 CFR Part 60 (40 FR 53340).

2.7 REVISION OF STANDARDS OF PERFORMANCE

Congress was aware that the level of air pollution control achievable by any industry may improve with technological advances. Accordingly, section 111 of the Act provides that the Administrator ". . . shall, at least every four years, review and, if appropriate, revise . . ." the standards. Revisions are made to assure that the standards continue to reflect the best systems that become available in the future. Such revisions will not be retroactive, but will apply to stationary sources constructed or modified after the proposal of the revised standards.

3. THE AIR OXIDATION INDUSTRY

3.1 GENERAL

The unit process of oxidation of organic compounds generally means the chemical reaction with an oxidizing agent to introduce one or more oxygen atoms into the compound, or to remove hydrogen or carbon atoms from the compound, or a combination of the above. This analysis deals with the subset of the oxidation industry in which air, or air enriched with oxygen, is the oxidizing agent.

This chapter describes the air oxidation industry structure, its production processes, and the associated emissions. The air oxidation industry consists of those facilities that produce chemicals included in the synthetic organic chemical manufacturing industry (SOCMI) by reacting one or more chemicals with oxygen supplied as air or air enriched with oxygen. This industry also includes chemicals produced using a combination of ammonia and air or of halogens and air as reactants. Processes that use pure oxygen as the reactant or that use an oxidizing agent other than oxygen are not considered in this study.

3.2 INDUSTRY STRUCTURE

It is difficult to separate the chemicals produced in air oxidation processes from other SOCMI products since air oxidation is not the only process to produce some of these chemicals.[1] Several commercial routes exist for many of these air oxidation chemicals including variations in organic feed, oxygen oxidation, or chemical oxidation. Also, many air oxidation chemicals are produced as intermediates for the manufacture of other chemicals. This section discusses the identification of the air oxidation chemicals, their uses and growth, and their domestic production.

3.2.1 Air Oxidation Chemicals

Thirty-six SOCMI chemicals have been identified as air oxidation chemicals. Table 3-1 lists these air oxidation chemicals; however, this list is not exclusive.

Each air oxidation chemical belongs to one of the following general chemical groups:

1. Acid anhydrides,
2. Alcohols,

TABLE 3-1. SOCMI CHEMICALS PRODUCED BY AIR OXIDATION

1. Acetaldehyde
2. Acetic Acid
3. Acetone
4. Acetonitrile
5. Acetophenone
6. Acrolein
7. Acrylic Acid
8. Acrylonitrile
9. Anthraquinone
10. Benzaldehyde
11. Benzoic Acid
12. 1,3-Butadiene
13. p-t-Butyl Benzoic Acid
14. n-Butyric Acid
15. Crotonic Acid
16. Cumene Hydroperoxide
17. Cyclohexanol
18. Cyclohexanone
19. Ethylene Dichloride
20. Dimethyl Terephthalate
21. Ethylene Oxide
22. Formaldehyde
23. Formic Acid
24. Glyoxal
25. Hydrogen Cyanide
26. Isobutyric Acid
27. Isophthalic Acid
28. Maleic Anhydride
29. Methyl Ethyl Ketone
30. α-Methyl Styrene
31. Phenol
32. Phthalic Anhydride
33. Propionic Acid
34. Propylene Oxide
    (tert butyl hydroperoxide)
35. Styrene
36. Terephthalic Acid

3. Aldehydes,
4. Alkenes,
5. Carboxylic acids,
6. Esters,
7. Ketones,
8. Nitriles,
9. Oxides,
10. Peroxides, or
11. Halogenated alkanes.

Of the 36 air oxidation chemicals identified, 11 are carboxylic acids. The remaining 25 chemicals include five ketones, five aldehydes, two alcohols, two acid anhydrides, three alkenes, three nitriles, two oxides, one ester, one peroxide, and one halogenated alkane.

Thirteen of the 36 chemicals contain an aromatic ring or rings. These 13 chemicals belong to each of the 11 groups listed above except the nitriles, oxides, and halogenated alkanes.

Most of these chemicals are structurally simple. The acid anhydrides, aldehydes, esters, and ketones, contain a carbonyl group. The alcohols, nitriles, oxides, and peroxides also contain reactive functional groups.[2]

The air oxidation chemicals have widely varying physical and chemical characteristics. They exist as solids, liquids, or gases at ambient condition, and most have characteristic odors.

3.2.2 Uses of Air Oxidation Chemicals

Air oxidation chemicals have many uses. They are used in production of plastics, textile fibers, rubber, surface coatings, dyes, food additives, fragrances, adhesives, drugs, and other substances.

There are two important characteristics of the air oxidation chemicals in general. First, many air oxidation chemicals serve as intermediate chemicals in the production of several other chemicals, which in turn have numerous end uses and final products. Second, while the number of uses of air oxidation chemicals is large, the major end uses are not very numerous. Plastics and textile fibers account for the bulk of production of the air oxidation chemicals studied here.[3] Table 3-2 lists the major use of each identified air oxidation chemical.[4,5]

TABLE 3-2. MAJOR END USE OF EACH IDENTIFIED SOCMI AIR OXIDATION CHEMICAL

1.	Acetaldehyde	Intermediates - Drugs - Polymers - Paints
2.	Acetic Acid	Intermediates - Polymers - Drugs - Solvents - Paints
3.	Acetone	Intermediates - Paints - Drugs - Solvent
4.	Acetonitrile	Solvent - Intermediates
5.	Acetophenone	Solvent - Drugs - Polymers - Paints
6.	Acrolein	Drugs - Intermediates
7.	Acrylic Acid	Polymers Paints
8.	Acrylonitrile	Polymers - Drugs
9.	Anthraquinone	Paints
10.	Benzaldehyde	Intermediates - Drugs - Paints
11.	Benzoic Acid	Drugs - Polymers - Paints
12.	1,3 Butadiene	Intermediate - Polymers
13.	p-t-Butyl Benzoic Acid	Intermediate
14.	n-Butyric Acid	Polymers - Drugs
15.	Crotonic Acid	Polymers - Drugs - Intermediates
16.	Cumene Hydroperoxide	Intermediate
17.	Cyclohexanol	Intermediate - Solvent
18.	Cyclohexanone	Intermediate - Solvent
19.	Ethylene Dichloride	Intermediate - Solvent
20.	Dimethyl Terephthalate	Polymers
21.	Ethylene Oxide	Drug - Intermediate
22.	Formaldehyde	Intermediate - Polymers - Solvent
23.	Formic Acid	Intermediate
24.	Glyoxal	Intermediate - Polymers
25.	Hydrogen Cyanide	Intermediate - Drugs
26.	Isobutyric Acid	Solvent - Drugs
27.	Isophthalic Acid	Polymers - Paints
28.	Maleic Anhydride	Polymers - Intermediate
29.	Methyl Ethyl Ketone	Solvent
30.	α-Methyl Styrene	Polymers
31.	Phenol	Polymers - Intermediate
32.	Phthalic Anhydride	Polymers - Drugs - Paints
33.	Propionic Acid	Drug
34.	Propylene Oxide	Intermediate
35.	Styrene	Polymer - Intermediate
36.	Terephthalic Acid	Polymers - Drugs - Paints

3.2.3 Companies and Production of Air Oxidation Chemicals

Fifty-nine companies produce one or more of the 36 air oxidation chemicals using an air oxidation process. Table 3-3 gives a listing of the companies and the chemicals produced by each company.[6,7] Of the 59 companies, 43 companies produce one or two chemicals; 14 produce from three to nine chemicals; and two produce 10 or more. Celanese Corporation and Monsanto each produce the largest number, 10.

A major share of the organic chemicals partially or fully produced by air oxidation processes are controlled by large multi-line chemical companies, chemical divisions, or subsidiaries of major oil companies, or multi-industry companies with chemical process operations. Table 3-4 gives the single, largest producer for each chemical and the percent of the chemical's total capacity owned by that company.[8,9] Other major producers are listed if the largest producer does not control a major share of the chemical's total production. Thirty-nine percent, or 14 out of 36 identified air oxidation chemicals, have an annual production greater than a billion pounds per year. Table 3-5 lists the annual air oxidation process production capacities of the identified air oxidation chemical.[10,11] In general, the higher the production volume of the air oxidation chemical, the less percent of total capacity any one company will own. Those chemicals that are produced by only one company are typically produced in small volumes.

3.2.4 Location of Air Oxidation Plants

There are currently 164 air oxidation process facilities operating in the United States. Forty-nine of these are located in ozone national ambient air quality standards (NAAQS) nonattainment areas. Table 3-6 gives a listing of the air oxidation manufacturing processes and the facilities employing each process.[12,13] The plant location, capacity, and major product(s) are given for each facility. Those facilities located in nonattainment areas are so indicated.

Although air oxidation industries are scattered throughout several states, many are located near refineries, which are located near domestic sources of oil or points of entry for imported oil. Some of the petrochemical plants border refineries, thus permitting an easy exchange of products. This results in a heavy concentration of chemical production along the

TABLE 3-3. COMPANIES PRODUCING SYNTHETIC ORGANIC CHEMICALS USING AIR OXIDATION PROCESSES

Company	Chemicals
Allied Chemical Co.	Acetone, Acetophenone, Cumene Hydroperoxide, α-Methyl Styrene, Phenol, Phthalic Anhydride
American Cyanamid Co.	Glyoxal
Amoco	Terephthalic Acid
Amoco-Standard Oil	Isophthalic Acid, Maleic Anhydride
Ashland Oil, Inc.	Maleic Anhydride
BASF Wyandotte Corp.	Phthalic Anhydride
Borden, Inc.	Formaldehyde
Celanese Corp.	Acetaldehyde, Acetic Acid, Acrylic Acid, n-Butyric Acid, Cyclohexanol, Cyclohexanone, Formaldehyde, Formic Acid, Methyl Ethyl Ketone, Propionic Acid
Chembond	Formaldehyde
Chevron Chemical Co.	Acetone, Phenol, Phthalic Anhydride
Ciba-Geigy Corp.	Hydrogen Cyanide
Clark Oil & Refining Corp.	Acetone, α-Methyl Styrene, Phenol
Continental Oil Co.	Ethylene Dichloride
Co-polymer Rubber and Chemical Corp.	1,3-Butadiene
Crompton & Knowles Corp.	Benzaldehyde
Degussa Corp.	Hydrogen Cyanide
Denka Chemical Co.	Maleic Anhydride
Diamond Shamrock	Ethylene Dichloride
Dow Badische Co.	Cyclohexanol, Cyclohexanone
Dow Chemical, USA	Acetone, Ethylene Oxide, Hydrogen Cyanide, Phenol, Ethylene Dichloride

TABLE 3-3 (Continued). COMPANIES PRODUCING SYNTHETIC ORGANIC CHEMICALS USING AIR OXIDATION PROCESSES

Company	Chemicals
DuPont	Acetonitrile, Acrylonitrile, Cyclohexanol, Cyclohexanone, Formaldehyde, Hydrogen Cyanide, Terephthalic Acid
Eastman Kodak Co.	Acetaldehyde, Acetic Acid, n-Butyric Acid, Crotonic Acid, Isobutyric Acid, Terephthalic Acid
Ethyl Corporation	Ethylene Dichloride
El Paso Natural Gas	1,3-Butadiene
Exxon Corp.	Phthalic Anhydride
Firestone Tire & Rubber Co.	1,3 Butadiene
GAF Corp.	Formaldehyde
General Electric	Acetone, Phenol
Georgia-Pacific Corp.	Acetone, Formaldehyde, α-Methyl Styrene, Phenol
Getty Oil Co.	Acetone, Acetophenone, α-Methyl Styrene, Phenol
B.F. Goodrich Chemical	Ethylene Dichloride
Gulf Oil Corp.	Formaldehyde
Hercofina	Dimethyl Terephthalate, Terephthalic Acid
Hercules, Inc.	Formaldehyde, Hydrogen Cyanide
Hocker	Formaldehyde
ICI Americas Inc.	Ethylene Dichloride
Inter'l Minerals & Chemical Corp.	Formaldehyde
Kalama Chemical, Inc.	Benzoic Acid, Phenol
Koppers Co., Inc.	Phthalic Anhydride
Monsanto Co.	Acetone, Acrylonitrile, Cyclohexanol, Cyclohexanone, Formaldehyde, Hydrogen Cyanide, Maleic Anhydride, Phenol, Phthalic Anhydride

TABLE 3-3 (Continued). COMPANIES PRODUCING SYNTHETIC ORGANIC CHEMICALS USING AIR OXIDATION PROCESSES

Company	Chemicals
Nipro, Inc.	Cyclohexanol, Cyclohexanone
Northwest Indust., Inc.	Benzoic Acid
Olin Corp.	Propylene Oxide
Oxirane Corp.	Propylene Oxide, Styrene
Pacific RC	Formaldehyde
Pfizer, Inc.	Benzoic Acid, Maleic Anhydride, Phenol
PPG Indust., Inc.	Ethylene Dichloride
Reichhold Chems., Inc.	Formaldehyde, Maleic Anhydride
Rohm and Haas Co.	Hydrogen Cyanide, Acrylic Acid
Shell Chemical Co.	Acetone, p-t-Butyl Benzoic Acid, Phenol, Ethylene Dichloride
Standard Oil Co. (OH)	Acetonitrile, Acrylonitrile, Hydrogen Cyanide
Stauffer Chemi. Co.	Ethylene Dichloride
Stepan Chemical Co.	Phthalic Anhydride
Tenneco, Inc.	Benzoic Acid, 1,3-Butadiene, Formaldehyde, Maleic Anhydride
Toms River Chemical Corp.	Anthraquinone
UOP, Inc.	Benzaldehyde
Union Carbide Corp.	Acetone, Acetophenone, Acrolein, Acrylic Acid Ethylene Oxide, Phenol, Propionic Acid, α-Methyl Styrene
U.S. Steel Corp.	Acetone, Cumene Hydroperoxide, Maleic Anhydride, α-Methyl Styrene, Phenol, Phthalic Anhydride
Vulcan Material Co.	Ethylene Dichloride
Wright Chemical Corp.	Formaldehyde

TABLE 3-4. LARGEST PRODUCERS OF IDENTIFIED SOCMI AIR OXIDATION CHEMICALS

Chemicals	Single Largest Producer	Percent of Total Capacity	Other Major Producers
Acetaldehyde	Celanese Corp.	68	-
Acetic Acid	Celanese Corp.	74	-
Acetone	Allied Chemical Corp.	17	Union Carbide Corp. Shell Chemical Co. Monsanto Co. Dow Chemical, USA U.S. Steel Chemicals
Acetonitrile	N/A	N/A	N/A
Acetophenone	N/A	N/A	N/A
Acrolein	Union Carbide Corp	100	-
Acrylic Acid	Rohm & Haas Co.	42	Celanese Chemical Union Carbide Corp.
Acrylonitrile	Monsanto Corp.	49	E.I. DuPont
Anthraquinone	Toms River Chemical Corp.	100	-
Benzaldehyde	N/A	N/A	N/A
Benzoic Acid	Kalama Chemical, Inc.	56	Northwest Indust., Inc.
1,3-Butadiene	Tenneco	57	El Paso Natural Gas
p-t-Butyl Benzoic Acid	Shell Chemical Co.	100	-
n-Butyric Acid	Eastman Kodak Co.	100	-
Crotonic Acid	Eastman Kodak Co.	100	-
Cumene Hydroperoxide	N/A	N/A	N/A
Cyclohexanol/ Cyclohexanone	E.I. DuPont de Nemours & Co., Inc. (E.I. DuPont)	40	Monsanto Co. -
Ethylene Dichloride	Dow Chemical Co.	35	Shell Chemical Co., PPG Industries, Inc. Diamond Shamrock Corp.
Dimethyl Terephthalate	Hercofina	75	-
Ethylene Oxide	Union Carbide Corp.	79	-
Formaldehyde	Celanese Corp.	20	Borden, Inc. E.I. DuPont Georgia-Pacific Corp.
Formic Acid	Celanese Corp.	100	-
Glyoxal	American Cyanamid	100	-

TABLE 3-4 (Continued). LARGEST PRODUCERS OF IDENTIFIED SOCMI AIR OXIDATION CHEMICALS

Chemicals	Single Largest Producer	Percent of Total Capacity	Other Major Producers
Hydrogen Cyanide	E.I. DuPont	53	Rohm and Haas Co.
Isobutyric Acid	Eastman Kodak Co.	100	-
Isophthalic Acid	Amoco-Standard Oil Co.	100	-
Maleic Anhydride	Monsanto Co.	24	Ashland Chemical Co. U.S. Steel Chemicals Amoco-Chemicals
Methyl Ethyl Ketone	Celanese Corp.	100	-
α-Methyl Styrene	Allied Chemical Corp.	45	U.S. Steel Chemicals
Phenol	Allied Chemical Corp.	18	Monsanto Co. Shell Chemical Co. U.S. Steel Chemicals Dow Chemical, USA Union Carbide Corp.
Phthalic Anhydride	Koppers Co., Inc.	26	Monsanto Co. U.S. Steel Corp. Stepan Chemical Co.
Propionic Acid	Union Carbide Corp.	100	-
Propylene Oxide	Oxirane Corp.	100	-
Styrene	Oxirane Corp.	100	-
Terephthalic Acid	Amoco	58	E.I. DuPont

N/A = Information not available.

TABLE 3-5. ANNUAL PRODUCTION CAPACITY OF THE IDENTIFIED SOCMI AIR OXIDATION CHEMICALS[f]

	Chemical	Capacity in Gigagrams Per Year
1.	Acetaldehyde	630
2.	Acetic Acid	770
3.	Acetone	950
4.	Acetonitrile	N/A
5.	Acetophenone	N/A
6.	Acrolein	27
7.	Acrylic Acid	428
8.	Acrylonitrile	880
9.	Anthraquinone	2[a]
10.	Benzaldehyde	N/A
11.	Benzoic Acid	145
12.	1,3-Butadiene	410
13.	p-t-Butyl Benzoic Acid	3[b,c]
14.	n-Butyric Acid	6[c,d]
15.	Crotonic Acid	6
16.	Cumene Hydroperoxide	N/A
17.	Cyclohexanol	e
18.	Cyclohexanone	925[e]
19.	Ethylene Dichloride	5888
20.	Dimethyl Terephthalate	890
21.	Ethylene Oxide	1430
22.	Formaldehyde	3900
23.	Formic Acid	7
24.	Glyoxal	N/A
25.	Hydrogen Cyanide	620
26.	Isobutyric Acid	5[c,d]
27.	Isophthalic Acid	66
28.	Maleic Anhydride	200
29.	Methyl Ethyl Ketone	40
30.	α-Methyl Styrene	24
31.	Phenol	1492

TABLE 3-5 (Continued). ANNUAL PRODUCTION CAPACITY OF THE IDENTIFIED SOCMI AIR OXIDATION CHEMICALS[f]

	Chemical	Capacity in Gigagrams Per Year
32.	Phthalic Anhydride	572
33.	Propionic Acid	86
34.	Propylene Oxide	181
35.	Terephthalic Acid	2235
36.	Styrene	635

N/A = Data not available.

[a] Letter from Bobsein, W.P., Toms River Chem. Corp., to Evans, L.B., EPA, February 11, 1980.

[b] Estimated based on data given in letter from Haxby, L.P., Shell Oil Co., to Evans, L.B., EPA, January 9, 1980.

[c] Memo from Galloway, J., EEA, to SOCMI Air Oxidation File. Estimation of capacities for p-t-Butylbenzoic Acid, n-Butyric Acid, and Isobutyric Acid from company data, April 9, 1981.

[d] Estimated based on data given in letter and attachment from Edwards, J.C., Eastman Kodak Co., to Evans, L.B., EPA, February 6, 1980.

[e] Production capacity of cyclohexanol and cyclonexanone have been reported together.

[f] Air oxidation capacity alone is given. Table 9-2 gives the total production capacity of these chemicals by all processes. Unless otherwise noted, 1981 data supplied by the Chemical Manufacturers' Association have been used (Reference 7).

TABLE 3-6. AIR OXIDATION PROCESS FACILITIES

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
	Acetaldehyde	Celanese Chemical	Bay City, Texas	136
	Acetaldehyde	Celanese Chemical	Clear Lake, Texas	295
	Acetaldehyde	Texas Eastman	Longview, Texas	200
	Acetic Acid (Wacker)	Celanese Chemical	Bay City, Texas	90
	Acetic Acid (Wacker)	Celanese Chemical	Clear Lake, Texas	227
	Acetic Acid/Formic Acid/MEK/Butyric Acid/Propionic Acid	Celanese Chemical	Pampa, Texas	298
	Acetic Acid (Wacker)	Tennessee Eastman	Kingsport, Tennessee	204
Yes	Acetone/Phenol	Allied Chemical	Frankford, Pennsylvania	446
Yes	Acetone/Phenol	Clark Chemical	Blue Island, Illinois	66
	Acetone/Phenol	Dow Chemical	Oyster Creek, Texas	338
	Acetone/Phenol	General Electric	St. Vernon, Indiana	290
	Acetone/Phenol	Georgia Pacific	Plaquemine, Louisiana	240
	Acetone/Phenol	Getty Refining	El Dorado, Kansas	70
Yes	Acetone/Phenol	Monsanto Chemical	Chocolate Bayou, Texas	363
Yes	Acetone/Phenol	Shell Chemical	Deer Park, Texas	363
Yes	Acetone/Phenol	Chevron	Richmond, California	40
	Acetone/Phenol	Union Carbide	Bound Brook, New Jersey	113
	Acetone/Phenol	Union Carbide	Penuelas, Puerto Rico	162
	Acetone/Phenol	U.S. Steel Chemical	Haverhill, Ohio	380
	Acrylic Acid	Celanese Chemical	Clear Lake, Texas	104
	Acrylic Acid	Celanese Chemical	Pampa, Texas	34
Yes	Acrylic Acid	Rohm and Haas	Deer Park, Texas	181
	Acrylic Acid/Acrolein	Union Carbide	Taft, Louisiana	136
	Acrylonitrile	DuPont	Memphis, Tennessee	140
	Acrylonitrile	DuPont	Beaumont, Texas	181
	Acrylonitrile	Monsanto Chemical	Alvin, Texas	240
	Acrylonitrile	Monsanto Chemical	Texas City, Texas	256
	Acrylonitrile	Vistron (SOHIO)	Lima, Ohio	200
Yes	Anthraquinone	Toms River Chemical	Toms River, New Jersey	1.8[a]

TABLE 3-6. AIR OXIDATION PROCESS FACILITIES (CONTINUED)

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
Yes	Benzaldehyde	Crompton and Knowles	Fair Lawn, New Jersey	Not Reported
	Benzoic Acid/Phenol	Kalama Chemical	Kalama, Washington	81
	Benzoic Acid/Phenol	Northwest Indust.	Beaumont, Texas	18
	Benzoic Acid/Phenol	Northwest Indust.	Chattanooga, Tennessee	23
	Benzoic Acid/Phenol	Pfizer Chemicals	Terre Haute, Indiana	15
Yes	Benzoic Acid/Phenol	Tenneco Chemicals	Garfield, New Jersey	7
	1,3-Butadiene	Firestone	Orange, Texas	54
Yes	1,3-Butadiene	Tenneco	Houston, Texas	236
	1,3-Butadiene	Copolymer Rubber and Chemical	Baton Rouge, Louisiana	27
	1,3-Butadiene	El Paso Natural Gas	Odessa, Texas	93
	p-t-Butylbenzoic Acid	Shell Chemical	Martinex, California	Not Reported, Estimated To Be 3.^{b,c}
	n-Butyric Acid	Tennessee Eastman	Kingsport, Tennessee	Not Reported, Estimated To Be 6.^{c,d}
	Crotonic Acid	Tennessee Eastman	Kingsport, Tennessee	6
	Cyclohexanone/Cyclohexanol	Badische	Freeport, Texas	140
	Cyclohexanone/Cyclohexanol	Celanese Chemical	Bay City, Texas	45
	Cyclohexanone/Cyclohexanol	DuPont	Orange, Texas	142
	Cyclohexanone/Cyclohexanol	DuPont	Victoria, Texas	231
	Cyclohexanone/Cyclohexanol	Monsanto Chemical	Pensacola, Florida	227
	Cyclohexanone/Cyclohexanol	Nipro	Augusta, Georgia	139

TABLE 3-6. AIR OXIDATION PROCESS FACILITIES (CONTINUED)

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
Yes	Terephthalic Acid (TPA)	DuPont	Old Hickory, Tennessee	213
	Terephthalic Acid (TPA)	DuPont	Wilmington, North Carolina	485
	Dimethyl Terephthalate (DMT)	Carolina Eastman	Columbia, South Carolina	227
	TPA	Tennessee Eastman	Kingsport, Tennessee	227
	DMT/TPA	Hercofina	Wilmington, North Carolina	703
	DMT	Hercofina	Spartanburg, South Carolina	75
	TPA	Amoco	Charleston, South Carolina	454
	TPA	Amoco	Decatur, Alabama	743
	Ethylene Oxide	Dow Chemical	Freeport, Texas	91
	Ethylene Oxide	Dow Chemical	Plaquemine, Louisiana	204
	Ethylene Oxide	Union Carbide	Seadrift, Texas	385
	Ethylene Oxide	Union Carbide	Taft, Louisiana	500
	Ethylene Oxide	Union Carbide Caribe	Ponce, Puerto Rico	250
	Formaldehyde (Silver)	Borden, Inc.	Demopolis, Alabama	45
	Formaldehyde (Silver)	Borden, Inc.	Diboll, Texas	36
	Formaldehyde (Silver)	Borden, Inc.	Fayetteville, North Carolina	107
Yes	Formaldehyde (Silver)	Borden, Inc.	Louisville, Kentucky	36
	Formaldehyde (Silver)	Borden, Inc.	Sheboygan, Wisconsin	59
Yes	Formaldehyde (Silver)	Borden, Inc.	Fremont, California	102
Yes	Formaldehyde (Silver)	Borden, Inc.	Kent, Washington	36
	Formaldehyde (Silver)	Borden, Inc.	La Grande, Oregon	30
	Formaldehyde (Silver)	Borden, Inc.	Missoula, Montana	40
	Formaldehyde (Silver)	Borden, Inc.	Springfield, Oregon	30
	Formaldehyde (Silver)	Borden, Inc.	Geismar, Louisiana	13
Yes	Formaldehyde (Mixed Metal)	Celanese Chemical	Newark, New Jersey	53
	Formaldehyde (Mixed Metal)	Celanese Chemical	Rock Hill, South Carolina	53
	Formaldehyde (Silver)	Celanese Chemical	Bishop, Texas	80
Yes	Formaldehyde (Silver)	E.I. DuPont Deremours	Belle, West Virginia	227
	Formaldehyde (Silver)	E.I. DuPont Denemours	Healing Springs, North Carolina	100
Yes	Formaldehyde (Silver)	E.I. DuPont Denemours	LaPorte, Texas	145
Yes	Formaldehyde (Silver)	E.I. DuPont Denemours	Linden, New Jersey	73
	Formaldehyde (Silver)	E.I. DuPont Denemours	Toledo, Ohio	122

TABLE 3-6. AIR OXIDATION PROCESS FACILITIES (CONTINUED)

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
	Formaldehyde (Mixed Metal)	GAF Corporation	Calvert City, Kentucky	45
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Albany, Oregon	45
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Columbus, Ohio	77
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Coos Bay, Oregon	35
	Formaldehyde (Silver)	Georgia-Pacific	Crossett, Arkansas	27
	Formaldehyde (Silver)	Georgia-Pacific	Crossett, Arkansas	45
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Lufkin, Texas	45
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Russelville, South Carolina	90
	Formaldehyde (Mixed Metal)	Georgia-Pacific	Taylorsville, Mississippi	55
	Formaldehyde (Silver)	Georgia-Pacific	Vienna, Georgia	45
	Formaldehyde (Mixed Metal)	Chembond	Andalusia, Alabama	32
	Formaldehyde (Mixed Metal)	Chembond	Springfield, Oregon	32
	Formaldehyde (Silver)	Chembond	Springfield, Oregon	32
	Formaldehyde (Mixed Metal)	Chembond	Winnfield, Alabama	32
	Formaldehyde (Mixed Metal)	Gulf Oil	Vicksburg, Mississippi	23
	Formaldehyde (Silver)	Hercules	Louisiana, Missouri	77
Yes	Formaldehyde (Mixed Metal)	International Minerals & Chemical	Seiple, Pennsylvania	120
Yes	Formaldehyde (Silver)	International Minerals & Chemical	Seiple, Pennsylvania	30
Yes	Formaldehyde (Silver)	Monsanto Chemical	Addyston, Ohio	55
	Formaldehyde (Silver)	Monsanto Chemical	Chocolate Bayou, Texas	88
	Formaldehyde (Silver)	Monsanto Chemical	Eugene, Oregon	45
Yes	Formaldehyde (Silver)	Monsanto Chemical	Springfield, Massachusetts	134
	Formaldehyde (Silver)	Hooker	North Tonawanda, New York	61
	Formaldehyde (Silver)	Reichhold Chemicals	Hampton, South Carolina	23
Yes	Formaldehyde (Mixed Metal)	Reichhold Chemicals	Houston, Texas	45
	Formaldehyde (Silver)	Reichhold Chemicals	Kansas City, Kansas	18
	Formaldehyde (Mixed Metal)	Reichhold Chemicals	Malvern, Arkansas	50
	Formaldehyde (Mixed Metal)	Reichhold Chemicals	Moncure, North Carolina	45
Yes	Formaldehyde (Mixed Metal)	Reichhold Chemicals	Tacoma, Washington	23
	Formaldehyde (Silver)	Reichhold Chemicals	Tuscaloosa, Alabama	34
	Formaldehyde (Mixed Metal)	Reichhold Chemicals	White City, Oregon	102
Yes	Formaldehyde (Mixed Metal)	Tenneco	Fords, New Jersey	57

TABLE 3-6. AIR OXIDATION PROCESS FACILITIES (CONTINUED)

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
Yes	Formaldehyde (Silver)	Tenneco	Fords, New Jersey	27
Yes	Formaldehyde (Silver)	Tenneco	Garfield, New Jersey	45
	Formaldehyde (Silver)	Pacific RC	Eugene, Oregon	43
	Formaldehyde (Mixed Metal)	Wright Chemical	Riegelwood, North Carolina	36
	Glyoxal	American Cyanamid	Charlotte, North Carolina	Not Reported
	Hydrogen Cyanide	Ciba-Geigy	St. Gabriel, Louisiana	40
	Hydrogen Cyanide	Degussa	Theodore, Alabama	24
	Hydrogen Cyanide	Dow Chemical	Freeport, Texas	9
	Hydrogen Cyanide	DuPont	Memphis, Tennessee	66
	Hydrogen Cyanide	DuPont	Orange, Texas	95
	Hydrogen Cyanide	DuPont	Victoria, Texas	95
	Hydrogen Cyanide	Ciba-Geigy	Glen Falls, New York	1
Yes	Hydrogen Cyanide	Monsanto	Texas City, Texas	63
	Hydrogen Cyanide	Rohm and Haas	Deer Park, Texas	90
	Isobutyric Acid	Tennessee Eastman	Kingsport, Tennessee	Not Reported, Estimated To Be 5.[c,d]
Yes	Isophthalic Acid	Amoco-Standard Oil	Joliet, Illinois	65
Yes	Maleic Anhydride (Benzene)	Ashland	Neal, West Virginia	27
Yes	Maleic Anhydride (Benzene)	Denka	Houston, Texas	23
Yes	Maleic Anhydride (Benzene)	Monsanto Chemical	St. Louis, Missouri	38
	Maleic Anhydride (Butane)	Monsanto Chemical	St. Louis, Missouri	10
Yes	Maleic Anhydride (Benzene)	Reichhold	Morris, Illinois	20
Yes	Maleic Anhydride (Butane)	Amoco-Standard Oil	Joliet, Illinois	27
Yes	Maleic Anhydride (Benzene)	Tenneco	Fords, New Jersey	10
	Maleic Anhydride (Benzene)	U.S. Steel Chemicals	Neville Island, Pennsylvania	36
	Maleic Anhydride (Benzene)	Pfizer	Terre Haute, Indiana	9

TABLE 3-6. AIR OXIDATION PROCESS FACILITIES (CONTINUED)

Nonattainment Area	Primary Air-Oxidation Product(s) (Manufacturing Process In Parentheses)	Company	Location	Capacity (Gg/yr) (Including All By-Products)
Yes	Phathalic Anhydride (Xylene)	Allied Chemical	El Segundo, California	16
Yes	Phathalic Anhydride (Xylene)	Basf Wyandotte	Kearny, New Jersey	68
	Phathalic Anhydride (Xylene)	Exxon	Baton Rouge, Louisiana	60
Yes	Phathalic Anhydride (Naphthalene)	Koppers	Bridgeville, Pennsylvania	40
Yes	Phathalic Anhydride (Xylene)	Koppers	Cicero, Illinois	107
Yes	Phathalic Anhydride (Naphthalene)	Monsanto Chemical	Bridgeport, New Jersey	40
	Phathalic Anhydride (Xylene)	Monsanto Chemical	Texas City, Texas	60
Yes	Phathalic Anhydride (Xylene)	Chevron	Richmond, California	23
	Phathalic Anhydride (Xylene)	Stepan	Millsdale, Illinois	76
Yes	Phathalic Anhydride (Naphthalene)	U.S. Steel	Neville Island, Pennsylvania	82
	Propionic Acid	Union Carbide	Texas City, Texas	86
Yes	Propylene Oxide/Styrene	Oxirane	Channelview, Texas	816
	1,2-Dichloroethane	Conoco Chemicals	Lake Charles, Louisiana	266
Yes	1,2-Dichloroethane	Diamond Shamrock	Deer Park, Texas	145
Yes	1,2-Dichloroethane	Diamond Shamrock	La Porte, Texas	454
	1,2-Dichloroethane	Dow Chemical	Freeport, Texas	726
	1,2-Dichloroethane	Dow Chemical	Osyter Creek, Texas	500
	1,2-Dichloroethane	Dow Chemical	Plaquemine, Louisiana	816
	1,2-Dichloroethane	Ethyl	Baton Rouge, Louisiana	318
Yes	1,2-Dichloroethane	Ethyl	Pasadena, Texas	118
	1,2-Dichloroethane	B.F. Goodrich Chemical	Calvert City, Kentucky	454
	1,2-Dichloroethane	ICI Americas Petrochemicals	Baton Rouge, Louisiana	234
	1,2-Dichloroethane	P.P.G. Industries Chemical-US	Lake Charles, Louisiana	703
Yes	1,2-Dichloroethane	Shell Chemical	Deer Park, Texas	635
	1,2-Dichloroethane	Shell Chemical	Norco, Louisiana	318
Yes	1,2-Dichloroethane	Stauffer Chemical	Long Beach, California	45
	1,2-Dichloroethane	Vulcan Chemicals	Geismar, Louisiana	159

[a] Op. cit., see Reference a for Table 2-5.

[b] Op. cit., see Reference b for Table 2-5.

[c] Op. cit., see Reference c for Table 2-5.

[d] Op. cit., see Reference d for Table 2-5.

Gulf Coast (Texas and Louisiana) and the East Coast, particularly in New Jersey and Pennsylvania.

Air oxidation plants are located in 27 states; over half of the 164 plants are located in the Gulf Coast and the East Coast. Twenty-eight of the 36 air oxidation chemicals are produced in Texas. Louisiana and New Jersey each produce 33 percent or more of the 36 air oxidation chemicals.

3.3 AIR OXIDATION PRODUCTION PROCESSES

The only determinant for classification as an air oxidation chemical is the process by which the chemical is produced. Some chemicals identified as air oxidation chemicals in Section 3.2.1 can be made by nonair oxidation processes.[14-16] Table 3-7 shows the percentages of air oxidation production of each of the chemicals.[17]

Despite the large variation in reaction types used to produce air oxidation chemicals, air oxidation processes can be grouped together because they have one very important characteristic in common, the need to vent large quantities of inert material containing VOC to the atmosphere. These inerts, predominantly nitrogen, are present because air contains 20.9 percent oxygen and 78.1 percent nitrogen by volume on a dry basis. The nitrogen in the air passes through the reaction unreacted. The exact quantity of nitrogen and unreacted oxygen emitted is a function of the amount of excess air used in the production process. The following sections present a discussion of the reaction types used for the production of air oxidation chemicals and the important factors which determine the amount of excess air used.

3.3.1 Reaction Types

The principal types of oxidation reactions that take place in the production of air oxidation chemicals are:

1. Dehydrogenation,
2. Introduction of an oxygen atom,
3. Destruction of carbon-carbon bonds,
4. Use of oxygen carrier,
5. Peroxidation,
6. Ammoxidation,
7. Oxidative condensation, and
8. Oxyhalogenation.

TABLE 3-7. PERCENTAGE PRODUCTION OF SOCMI CHEMICALS BY AIR OXIDATION

Product	% of Product Manufactured by Air Oxidation
1. Acetaldehyde	99.7
2. Acetic Acid	40
3. Acetone	65
4. Acetonitrile	No Data
5. Acetophenone	No Data
6. Acrolein	52
7. Acrylic Acid	94
8. Acrylonitrile	100
9. Anthraquinone	No Data
10. Benzaldehyde	No Data
11. Benzoic Acid	100
12. 1,3-Butadiene	23
13. p-t-Butyl Benzoic Acid	No Data
14. n-Butyric Acid	No Data
15. Crotonic Acid	No Data
16. Cumene Hydroperoxide	No Data
17. Cyclohexanol	81
18. Cyclohexanone	81
19. 1,2-Dichloroethane	96
20. Dimethyl Terephthalate	100
21. Ethylene Oxide	51
22. Formaldehyde	100
23. Formic Acid	23
24. Glyoxal	No Data
25. Hydrogen Cyanide	100
26. Isobutyric Acid	No Data
27. Isophthalic Acid	100
28. Maleic Anhydride	80
29. Methyl Ethyl Detone	11[a]
30. α-Methyl Styrene	100[a]
31. Phenol	98
32. Phthalic Anhydride	100
33. Propionic Acid	62[a]
34. Propylene Oxide	20
35. Styrene	18
36. Terephthalic Acid	100

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*Produced by air or oxygen oxidation.

[a] SRI International 1978 Directory of Chemical Producers, United States of America.

Dehydrogenation is illustrated in the transformation of a primary alcohol to an aldehyde:

$$C_2H_5OH + \frac{1}{2}O_2 = CH_3CHO + H_2O$$

or of a secondary alcohol to a ketone:

$$CH_3CHOHCH_3 + \frac{1}{2}O_2 = CH_3COCH_3 + H_2O$$

or of an alkane to alkene:

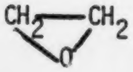
$$CH_3CH_2CH_2CH_3 + O_2 = CH_2CHCHCH_2 + 2H_2O$$

An atom of oxygen may be introduced into a molecule, as is illustrated by the oxidation of an aldehyde to an acid:

$$CH_3CHO + \frac{1}{2}O_2 = CH_3COOH$$

or of a hydrocarbon to an oxide:

$$CH_2CH_2 + \frac{1}{2}O_2 =$$



A combination of the above may occur, as in the preparation of aldehydes from hydrocarbons:

$$CH_4 + O_2 = CH_2O + H_2O$$

or of benzoic acid from toluene:

$$C_6H_5CH_3 + 1\frac{1}{2}O_2 = C_6H_5COOH + H_2O$$

A combination of dehydrogenation, oxygen introduction, and destruction of carbon-carbon bond may all occur in the same process of oxidation, e.g., in the oxidation of naphthalene to phthalic anhydride:

$$C_{10}H_8 + 4\frac{1}{2}O_2 = C_8H_4O_3 + 2H_2O + 2CO_2$$

Oxidation may be accomplished indirectly through the use of intermediate or oxygen carrier:

$$C_2H_4 + 2CuCl_2 + H_2O \xrightarrow{PdCl_2} CH_3CHO + HCl + 2CuCl$$

Peroxidation occurs readily under certain conditions. Thus, some reactions occur directly with air when catalyzed by heavy metal salts:

Cumene + air = Cumene Hydroperoxide

Ammoxidation is a process for the formation of nitriles by the action of ammonia in the presence of air or oxygen on olefins, organic acids, or other alkyl group of alkylated aromatics:

$$C_3H_6 + NH_3 + 1\frac{1}{2}O_2 = CH_2CHCN + 3H_2O$$

Oxidative condensation occurs when two molecules combine with each other with the introduction of oxygen atoms and removal of small molecules like water:

$$2CH_3CHO + O_2 = CH_3COOOCCH_3 + H_2O$$

Oxyhalogenation is a process in which oxygen and a halogen reacts with an organic compound:

$$C_2H_4 + \frac{1}{2}O_2 + 2HCl = ClCH_2CH_2Cl + H_2O$$

In some reactions, several types of oxidation take place at the same time resulting in co-products and by-products. A co-product is formed simultaneously along with the desired reaction product and is primarily marketable. A common example of such a reaction would be air oxidation of cyclohexane, where cyclohexanol and cyclohexanone are produced as co-products.[18] By-products, on the other hand, result from competitive side or parallel reactions occurring along with the main reaction. It is generally a "leftover" of the process, which in some cases is marketable. For example, in the manufacture of acrylonitrile by ammoxidation of propylene, acetonitrile and hydrogen cyanide are produced as by-products.[19] Also, in some cases, the product of the air oxidation reaction is not the end product of the production process, such as the production of ethylbenzene hydroperoxide which is used to make styrene. Table 3-8 lists co-products and by-products for those air oxidation processes with more than one product.

3.3.2 Raw Materials

The principal raw materials for the manufacture of air oxidation chemicals are olefins (ethylene and propylene), C_4 fractions (butanes and butenes) and aromatics. Table 3-9 shows the air oxidation chemicals divided into these categories. Because of the vast number of different synthesis routes available, several of the air oxidation chemicals fall into more than one classification.

TABLE 3-8. AIR OXIDATION PROCESSES WITH CO-PRODUCT(S) AND BY-PRODUCT(S)

Process	Co-Products	By-Products
Butane Oxidation II	Acetic Acid, Methyl Ethyl Ketone	Formic Acid, n-Butyric Acid, Propionic Acid
Cyclohexane Oxidation	Cyclohexanol, Cyclohexane	
Ethylbenzene Hydroperoxidation	Styrene, Propylene Oxide	
Cumene Hydroperoxidation	Acetone, Phenol	Cumene Hydroperoxide, Acetophenone, α-Methyl Styrene
Toluene Oxidation	Phenol, Benzoic Acid	
p-Xylene Oxidation	Dimethyl Terephthalate, Terephthalic Acid	
Propylene Oxidation	Acrylic Acid	Acrolein
Propylene Ammoxidation	Acrylonitrile, Hydrogen Cyanide	Acetonitrile

TABLE 3-9. BASIC RAW MATERIALS FOR AIR OXIDATION CHEMICALS

Ethylene Based	Propylene Based	Butane Based	Aromatic Based	Other
Acetaldehyde	Acrolein	Acetic Acid	Acetone	Formaldehyde (Methanol from Syngas)
Acetic Acid	Acrylic Acid	1,3-Butadiene	Acetophenone	Hydrogen Cyanide (Methane + Ammonia)
Ethylene Oxide		n-Butyric Acid	Benzaldehyde	Hydrogen Cyanide (Ammonia + Propylene)
Glyoxal		Formic Acid	Benzoic Acid	Acetonitrile (Ammonia + Propylene)
Crotonic Acid		Isobutyric Acid	para-tert-Butyl Benzoic Acid	Acrylonitrile (Ammonia + Propylene)
		Maleic Anhydride	Cumene Hydroperoxide	
		Methyl Ethyl Ketone	Cyclohexanol	
		Propionic Acid	Cyclohexanone	
			Dimethyl Terephthalate	
			Isophthalic Acid	
			Maleic Anhydride	
			Methyl Styrene	
			Phenol	
			Phthalic Anhydride	
			Styrene	
			Terephthalic Acid	

In air oxidation processes, there is a large contribution of feedstock to overall price of the chemical, and thus, there exists a strong incentive to find cheaper (or less refined) or more readily available feedstocks. This can be seen in the gradual switch to butane feedstock in the manufacture of maleic anhydride. Originally, maleic anhydride was produced via air oxidation of benzene. With the increase in benzene costs, many new maleic anhydride plants have switched to n-butane feeds.[20] Another reason for the switch from benzene to n-butane feed for maleic anhydride would be the additional cost to meet the proposed NESHAP regulation on benzene.

Butanes can be obtained from natural gas, from crude oil, or as a by-product of olefins production. Aromatics can be obtained from oil as a product of catalytic reforming or from coal as a by-product of coking. At present, the largest source is from catalytic cracking during oil refining, however, this may change in the future as more synthetic fuel plants based on coal are built. Several of the air oxidation chemicals are made from natural gas-based petrochemicals. Alternative routes to these chemicals utilizing oil-based feeds are being developed.

3.3.3 Reaction Characteristics

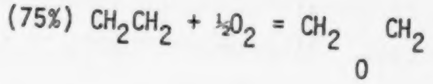
In spite of numerous reaction mechanisms, all air oxidation processes vent large quantities of inert material containing predominantly nitrogen from air and some VOC. Therefore, to quantify VOC emissions, and to select the applicable control method, it is necessary to quantify offgas flow and VOC concentrations. As discussed in Chapter 4, flow and VOC concentrations are the major process parameters which determine the costs of controlling VOC emissions by thermal or catalytic incineration. This section discusses the reaction characteristics which affect the offgas flow from air oxidation processes. Section 3.4 presents the results of the statistical analysis from which the national VOC emissions profile were developed.

There are several reaction characteristics which determine the amount of offgas vented to the atmosphere. They are as follows:

1. Reaction stoichiometry,
2. Reaction phase, and
3. Explosion hazard.

3.3.3.1 Reaction Stoichiometry

In air oxidation reactions, oxygen from the air reacts with an organic reactant to produce the following: (1) product air oxidation chemical, (2) some carbon dioxide and carbon monoxide due to partial combustion of the feedstock, and (3) co-products and by-products. The total oxygen required is dependent on the extent of each reaction. The stoichiometry of the reaction and the catalyst selectivity of a process determine the theoretical amount of oxygen required for a given process. Catalyst selectivity is defined as the quotient of the amount of reaction product to the amount of converted feedstock.[21] For example, in the ethylene oxide process, ethylene reacts with oxygen to produce ethylene oxide (main reaction) and carbon dioxide according to the following equations:



$$(75\%)\ CH_2CH_2 + \tfrac{1}{2}O_2 = CH_2 \underset{O}{\quad} CH_2$$

$$(25\%)\ CH_2CH_2 + 3O_2 = 2CO_2 + 2H_2O$$

$$(100\%)\ CH_2CH_2 + \frac{9}{8}\,O_2 = \frac{3}{4}\,C_2H_4O + \tfrac{1}{2}CO_2 + \tfrac{1}{2}H_2O$$

The catalyst selectivity is 75 percent.[23] The molecular oxygen ratio (MOR), defined as moles of oxygen per mole of product, is 0.5 for the main reaction. However, considering the oxygen required for the complete combustion side reaction, and the average catalyst selectivity of 75 percent[22], the MOR of the overall reaction becomes 1.5.

Generally, all air oxidation processes require greater than stoichiometric amount of air to realize optimum conversion, favorable reaction rates, and to prevent explosion hazard.

3.3.3.2 Reaction Phase

Generally, air oxidation reaction can be carried out in either liquid or gas phase. Table 3-10 shows the division of the various air oxidation processes between liquid and vapor phase. The processes are categorized according to the phase of the air oxidation reaction step, and not according to the phase of the step(s) in which the final product(s) is/are formed.

TABLE 3-10. PHASE OF THE AIR OXIDATION REACTION STEP IN THE PRODUCTION OF AIR OXIDATION CHEMICALS

Liquid Phase

1. Acetaldehyde
2. Acetic Acid
3. Acetone
5. Acetophenone
6. Benzaldehyde
7. Benzoic Acid
8. p-t-Butyl Benzoic Acid
9. n-Butyric Acid
10. Cumene Hydroperoxide
11. Cyclohexanol
12. Cyclohexanone
13. Dimethyl Terephthalate
14. Formic Acid
15. Isobutyric Acid
16. Isophthalic Acid
17. Methyl Ethyl Ketone
18. α-Methyl Styrene
19. Phenol
20. Propionic Acid
21. Propylene Oxide (tert butyl hydroperoxide)[a]
22. Styrene[a]
23. Terephthalic Acid

Vapor Phase

1. Acetaldehyde
2. Acetonitrile
3. Acrolein
4. Acrylic Acid
5. Acrylonitrile
6. Anthraquinone
7. 1,3-Butadiene
8. Ethylene Dichloride
9. Ethylene Oxide
10. Formaldehyde
11. Glyoxal
12. Hydrogen Cyanide
13. Maleic Anhydride
14. Phthalic Anhydride

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[a] The air oxidation step in styrene/propylene oxide manufacture is the liquid phase hydroperoxidation of ethylbenzene.

Liquid phase reactions generally utilize high molecular weight thermally unstable reactants. The reaction temperatures are low or moderate and usually require high pressures for optimum reaction rates.[23] The extent of oxidation is controlled by limiting the duration of operation, controlling the temperature and using low excess air. Large amounts of excess air may cause branching of radical precursors with formation of a multiplicity of radicals and, consequently, runaway reactions which could ultimately result in explosion.

The catalyst used in liquid phase processes may be either dissolved or suspended in finely divided form to ensure contact with the bubbles of gas-containing oxygen which pass through the liquid undergoing oxidation. To speed up the production, means must be provided for initially raising the temperature and for later removing reaction heat. Heat may be removed and temperature controlled by circulation of either the liquid being oxidized or a special cooling fluid through the reaction zone and then through an external heat exchanger. Where low temperatures and slow reaction rates are indicated, natural processes of heat flow to the atmosphere may suffice for temperature control.

In addition, liquid phase processes require adequate mixing and contact of the two immiscible phases of gaseous oxidizing agent and the liquid being oxidized. Mixing may be obtained by the use of special distributor inlets for the air, designed to spread the air throughout the liquid. Mechanical stirring or frothing of the liquid are the other methods of providing thorough mixing.

Figure 3-1 represents a schematic flowsheet of a liquid phase air oxidation process. Liquid feedstock and catalyst are fed into a reactor. The reaction is carried out by passing air through this liquid mixture at a controlled temperature and pressure. After completion of the reaction, two streams come out of the reactor, liquid and gaseous. The liquid stream usually contains the desired product, which is taken to a product recovery system consisting of a series of different unit operations (e.g., distillation, crystallization, evaporation, etc). The gaseous stream containing nitrogen, unreacted oxygen, CO_2, and some VOC is condensed or cooled and then fed into the gas separator to recover the condensable compounds before venting it to the atmosphere.

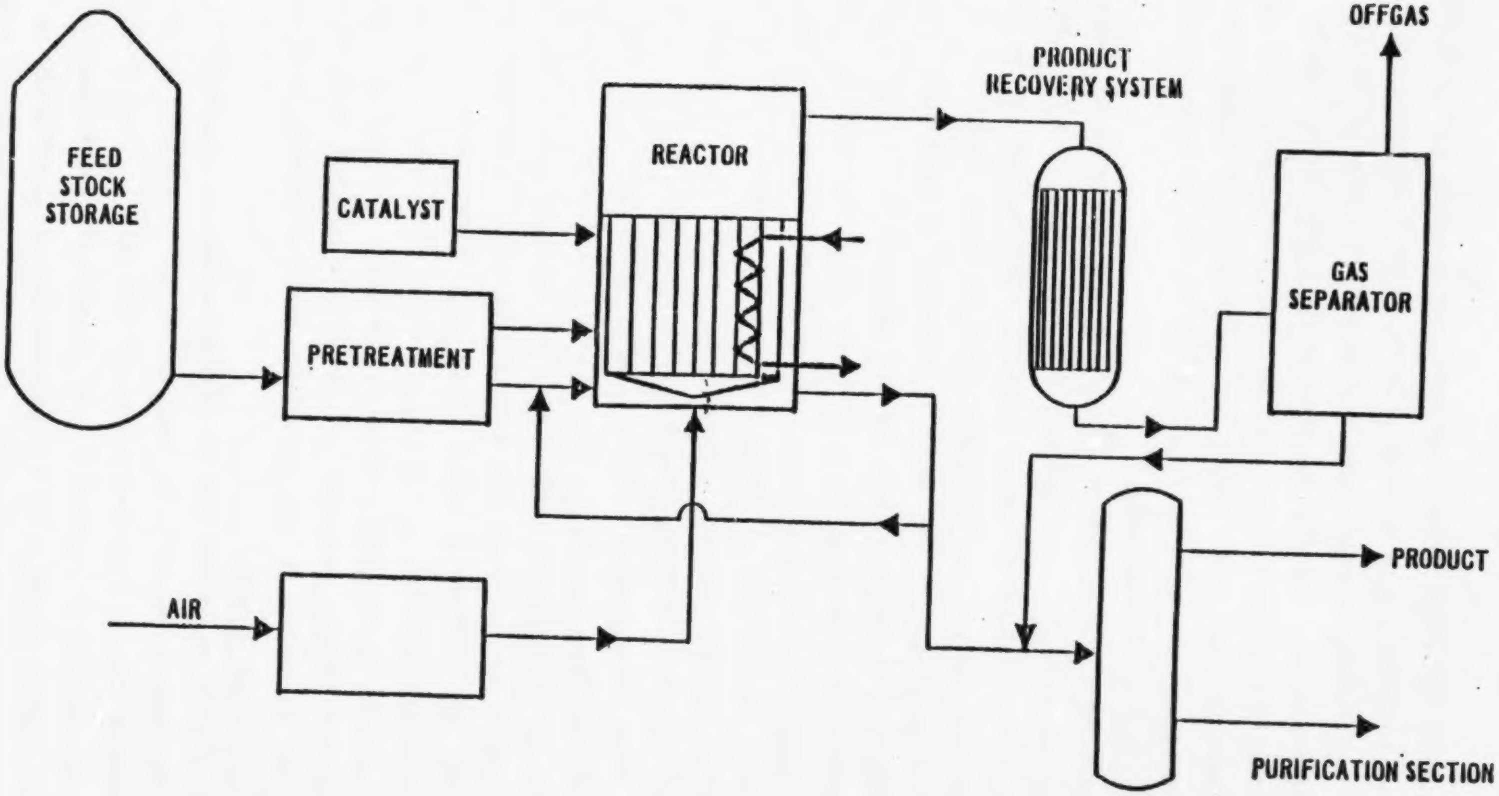
FEED
STOCK
STORAGE
CATALYST
PRETREATMENT
AIR
REACTOR
PRODUCT
RECOVERY SYSTEM
OFFGAS
GAS
SEPARATOR
PRODUCT
PURIFICATION SECTION

Figure 3-1. Schematic of a flowsheet for a liquid phase air oxidation process.

In contrast to liquid phase reactions, vapor phase air oxidation reactions can be effectively applied only to readily volatile substances that are of sufficient thermal stability to resist dissociation at elevated temperatures. The desired product must also be thermally stable to continued oxidation and must be readily separable from gaseous product. These various restrictions limit the material capable for economic processing by vapor phase air oxidation to the simpler aliphatic and aromatic series of compounds.[24]

In vapor phase air oxidation processes, a solid or vapor phase catalyst may be employed. The temperatures are usually high. Control is affected by limiting the time of contact, temperature, proportion of oxygen, type of catalyst, or by combinations of these factors.

By their very nature, the vapor phase oxidation processes result in the concentration of reaction heat in the catalyst zone, from which it must be removed in large quantities at high temperature levels. Removal of heat is essential to prevent destruction of apparatus, catalyst, or raw material. Maintenance of temperature at the proper level is necessary to ensure the correct rate and degree of oxidation.[25] Figure 3-2 represents a schematic flowsheet of a vapor phase air oxidation process. The feedstock which is either in vapor or liquid phase is first vaporized, if required, and then mixed with air in a mixing chamber. The mixture is then fed at the required temperature and pressure into a reaction chamber where it comes in contact with a catalyst. After completion of the reaction, the mixture of gases coming out of the reactor is passed through a product recovery system consisting of different unit operations, which can include condensers, scrubbers, or both. The exhaust gas coming from the product recovery system containing predominantly nitrogen and some VOC, is vented to the atmosphere or to a control device.

3.3.3.3 Explosion Hazard

Many organic reactants used in air oxidation processes are inflammable and require adequate means to prevent explosion hazard. When vapors of an inflammable organic compound are mixed with air in the proper proportion, ignition can produce an explosion. An increase in temperature of a mixture of organic vapors with air expands the range of organics concentration capable of leading to an explosion. Because of the explosion hazard,

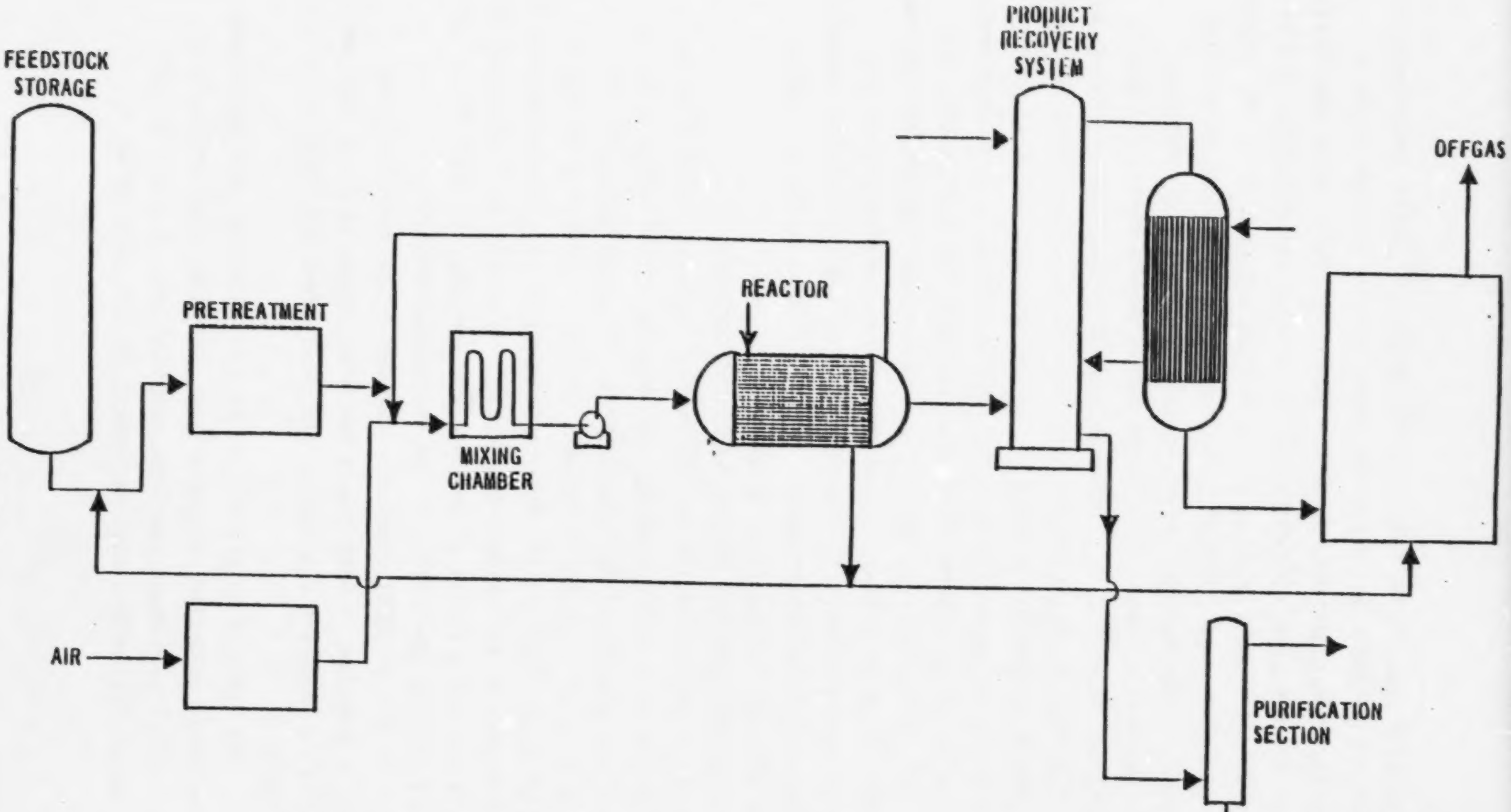
FEEDSTOCK STORAGE
PRETREATMENT
MIXING CHAMBER
REACTOR
PRODUCT RECOVERY SYSTEM
OFFGAS
AIR
PURIFICATION SECTION
PRODUCT

Figure 3-2. Schematic of a flowsheet for a vapor phase air oxidation process.

many insurance regulations limit the inflammable organics concentration to 25 percent of the lower explosive limit in air. In some cases to maintain reaction conditions below the explosive limit, large quantities of excess air are used. Alternatively, low inlet concentrations can be achieved by recycling a portion of the reactor offgas back to the reactor system. Some processes, however, can operate above the explosive limit. For example, in the manufacture of formaldehyde by silver catalyst process, methanol concentration in the gas stream is maintained above the explosive limit.[26] It is, however, possible that some processes, by use of fluidized bed reactors, gas stream recycle, or utilizing sophisticated heat transfer systems may operate within the apparent explosive range.[27]

The explosion hazard of an air oxidation process is also dependent on the autoignition temperature of the reactants and the product. The autoignition temperature is defined as that minimum temperature required to initiate or cause self-sustained combustion independently of the heating or heated element.[28] Compounds having low autoignition temperature would require better heat removal. The use of high excess air again provides a method of realizing adequate heat removal.

3.4 STATISTICAL ANALYSIS OF AIR OXIDATION PROCESSES

In this section, results of statistical analysis of existing air oxidation processes are presented. One purpose of the analysis is to develop a nationwide VOC emission profile. A second purpose is to determine a valid predictor for excess air in air oxidation processes. The analysis was based on the data collected from 59 plants producing 14 SOCMI chemicals by air oxidation processes. The details of the statistical procedure and the analysis of the data are presented in Appendix F. The following are the conclusions of the statistical analysis.

1. Of the 13 SOCMI chemicals included in the data base, one chemical is produced in both liquid and vapor phase; while of the remaining 12 chemicals, seven are produced in the vapor phase and five in the liquid phase.

2. The ratio of excess air to the stoichiometric air requirement for vapor phase oxidation processes range from less than one to 13.

3. All liquid phase reactions examined have the ratio of excess air to the stoichiometric air requirement of less than three.

4. Excess air requirement is influenced by reaction stoichiometry, reaction temperature, autoignition temperatures, and explosive limits.

5. As discussed in Appendix F, the amount of excess air required for vapor phase air oxidation processes can be predicted by the equation:

$$F = C_1 \; (T_R/T_i) + C_2 \; (1/EL) + C_3 \;\; T_R/(T_i EL) \;\; + C_4 \;\; (EL)$$

where:

C_1, C_2, C_3, C_4 = Constants.

T_R = Reaction temperature (°C).

T_i = Lowest autoignition temperature (°C) of any reaction reactant or product.

EL = Lower explosive limit (volume percent) of most explosive reactant or product. (If reaction is run above the upper explosive limit, then the upper explosive limit is used.)

$F = \frac{\text{Actual Offgas Flow}}{\text{Stoichiometric Input Air}}$.

6. Of the 44 plants producing SOCMI chemicals in the vapor phase, the distribution of flows, VOC, and heat content shows that 35 plants have streams with less than 1.0 volume percent VOC; 38 plants have flows less than 50,000 scfm and 18 plants have streams with less than 20 Btu/scf heat content. The maximum VOC content is 2.2 volume percent, the maximum flow is 126,000 scfm, and the maximum heat content is 114 Btu/scf.

7. Of the 15 plants producing SOCMI chemicals in the liquid phase, the distribution of flows, VOC, and heat content shows that eight plants have streams with less than 0.1 volume percent VOC, seven plants have flow less than 10,000 scfm, and 14 plants have streams with less than 20 Btu/scf heat content. The maximum VOC content is 0.76 volume percent, the maximum flow is 64,000 scfm, and the maximum heat content is 41 Btu/scf.

3.4.1 National Emissions Profile

Air oxidation facilities use 36 types of oxidation processes (23 principal processes and 13 specialty processes) to manufacture 36 different organic chemicals. Because of the number and diversity of facilities and processes in the air oxidation industry, the traditional model plant approach was not used. Because of the number and diversity of facilities and manufacturing processes in the air oxidation industry, a large number of model plants would have been required in order to accurately determine the environmental, energy, and cost impacts associated with the regulatory alternatives. However, as discussed in Chapter 4, only a limited amount of vent stream data is required to determine incinerator costs and efficiency. The required data include offgas flowrate, net heating value, and hourly VOC emissions, and whether the offgas contains halogenated compounds. Therefore, although data from many types of processes are still required in order to adequately represent the air oxidation industry, the data need not consist of fully designed model plants. Rather, a national statistical profile of air oxidation processes was constructed. The national profile characterizes air oxidation processes according to national distributions of the three critical offgas parameters for halogenated and nonhalogenated vent streams. The regulatory alternative environmental, energy, and cost impacts are therefore evaluated as impacts upon the entire population of affected facilities, as represented by the national profile. The development and statistical basis for the national profile are described in detail in Appendix F.

The actual use of the national statistical profile assumes that the distribution of offgas flowrate, VOC emission rate, corrosion properties, and stream net heating value is chemical independent. Chemical identities are not considered in the profile, nor is there claimed to be a one-to-one correspondence between any one data vector and an existing offgas stream. It is assumed, however, that the overall proportions and distributions of the parameter values and data vectors be similar to those of the existing population of air oxidation facilities. Thus, since the national statistical profile contains 59 data vectors, each data vector and associated impacts of population control represents 1/59 of the existing population to be analyzed for control.

The national emissions profile was constructed using emissions data from the Houdry questionnaire.[29] The questionnaire covered 13 major air oxidation chemicals. These chemicals are shown in Table 3-11. A total of 59 air oxidation plants are represented by the Houdry data, which is about 36 percent of the total air oxidation plants in existence today.

TABLE 3-11. CHEMICALS COVERED BY HOUDRY QUESTIONNAIRE

Chemical	Process	Number of Plants
Acetaldehyde	Ethanol	1
	Ethylene	1
Acetic Acid	Butane	1
Acrylonitrile	Propylene	4
Cyclohexanone/Cyclohexanol	Cyclohexane	3
Dimethyl Terephthalate	p-Xylene, Methanol	2
Ethylene Dichloride	Oxychlorination	9
Ethylene Oxide	Ethylene	4
Formaldehyde	Methanol Silver Catalyst	9
Formaldehyde	Methanol Mixed Metal	4
Hydrogen Cyanide	Ammoxidation Methane	1
Maleic Anhydride	Benzene	7
Phenol	Cumene	6
Phthalic Anhydride	Naphthalene	2
	o-Xylene	3
Terephthalic Acid	p-Xylene	2

3.5 BASELINE EMISSIONS AND CONTROL LEVEL

Baseline control levels refers to the level of control to which any new sources would be subject without the new source performance standard (NSPS). This control level was estimated based on two factors. The first is the degree of emissions control resulting from air pollution control currently required under State implementation plans (SIP's) and other existing regulations. The second factor is the level of control projected to be required under modified SIP's, in ozone NAAQS nonattainment areas requesting extension, which would reflect the level of control recommended in the SOCMI air oxidation CTG. The choice of baseline emissions control level has a direct impact on the magnitude of cost, energy, and environmental impacts of any NSPS. Because of the large number of chemicals covered by the air oxidation standard, it is difficult to assess the level of baseline emissions control attributable to either SIP's or current emissions control practiced by industry for other reasons, e.g., product recovery, odor abatement, etc. For the purpose of this analysis, current SIP's and those projected to be in force to reflect the air oxidation CTG, are used to define the baseline.

Air oxidation facilities are located all over the United States and are subject to many different SIP's. Over 90 percent of the total SOCMI production capacity is located in 14 States, with Louisiana and Texas contributing more than half the production capacity. Of the 14 States, only Texas, Louisiana, New Jersey, and Illinois have VOC emission regulations applicable to SOCMI air oxidation processes. Texas requires facilities emitting more than either 100 lbs/day or 250 lbs/hr, depending on the true vapor pressure of the VOC, to "properly" incinerate the waste gas stream at 1300^{0}F. This is equivalent to approximately 85 percent VOC reduction.[30] Louisiana also requires incineration of VOC at 1300^{0}F, with a 0.3 second residence time, or control by other acceptable methods; however, control requirements may be waived if the offgas is not significant or will not support combustion without auxiliary fuel.[31] New Jersey uses a sliding scale, based on the degree of difficulty in controlling the VOC emission source, to establish allowable emission rates for individual sources. Depending on the vapor pressure, concentration, and amount of the waste stream VOC, the New Jersey regulation requires from 0 to 99.7 percent VOC reduction.[32] Illinois does not differentiate between organic solvents and organic compounds in an applicable regulation that limits VOC emissions to eight lbs/hr unless these emissions are reduced by 85 percent.[33] The remaining 10 States do not have regulations for control of air oxidation VOC emissions.

Information concerning air oxidation production capacity and VOC emissions can be used to select a national baseline emission control level based on the control requirements under existing and projected CTG-based regulations. However, only some States currently require VOC control at air oxidation facilities, so assuming that all States require a similar VOC reduction (e.g., 85 percent) understates the projected impacts of the NSPS. Therefore, a weighted average of current control requirements and projected regulations based on the CTG provides the closest approximation of VOC control levels without the NSPS. Analysis shows that the weighted average VOC emissions reduction attributable to the existing and projected SIP's is 72 percent. This analysis assumes that the national profile adequately represents the projected new source population of plants in each State with an applicable SIP, as well as the total population. The method of estimating the baseline control fraction is discussed in more detail in Appendix F.

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4. EMISSION CONTROL TECHNIQUES

4.1 INTRODUCTION

This chapter describes the control techniques and associated emission reduction effectiveness for air oxidation unit process vents of the synthetic organic chemical manufacturing industry (SOCMI). The effectiveness of combustion systems is examined with respect to their principles of operation, advantages, and disadvantages.

The SOCMI process vent streams show a great variety in volume flows, chemical compositions, and volatile organic compound (VOC) concentrations. This chapter concentrates on thermal oxidation since it is a VOC control method universally applicable to SOCMI air oxidation vent streams, although it is not necessarily the best for a given process.

Effectiveness and specificity of condensers, absorbers, adsorbers, and catalytic oxidizers may be affected by changes in waste stream conditions. These conditions include flowrate, VOC concentration, chemical and physical properties of VOC, waste stream contaminants, and waste stream temperature. Analysis of air oxidation VOC emissions control by these methods would be unwieldy. Also, control systems based on condensation or absorption are generally used as product recovery devices, and the removal efficiencies decrease as the VOC concentrations decrease.

Thermal oxidation, however, is much less dependent on process and waste stream conditions than the other control techniques. It is the only demonstrated VOC control which is applicable to all SOCMI air oxidation processes. Incinerator cost and efficiency determinations require a limited amount of vent stream data (volume flow, VOC emission rate, net heating valve, andcorrosion properties). The choice of thermal oxidation as the single control technique for analysis yields conservative estimates of energy, economic, and environmental impacts since thermal oxidation is relatively expensive and energy-intensive.

All new incinerators, if properly designed, adjusted, maintained, and operated, can achieve at least a 98 percent VOC reduction or 20 ppmv exit concentration, whichever is less stringent. This control level can be achieved by incinerator operation at conditions which include a maximum of 1600^{O}F and 0.75 second residence time.

Process modification, improvements in product recovery, and use of additional control devices are possible routes to lower emission levels. This chapter discusses the advantages and disadvantages of using product recovery devices such as absorbers, adsorbers, and condensers alone, or in conjunction with VOC control devices such as boilers and thermal and catalytic oxidizers to achieve reduction of VOC emissions. Detailed descriptions and efficiency data are available in Appendix A and in the references.

Boilers can be useful as VOC control devices only when the waste gas stream volume flow is not large enough to upset the combustion process. Furthermore, the waste gas stream must either have sufficient oxygen to be used as combustion air or have a sufficiently high heating value to be used as part of the fuel input. Air oxidation processes which currently employ a boiler or process heater for VOC control include the Andrussow process for manufacture of hydrogen cyanide, maleic anhydride from benzene, acrylonitrile, and formaldehyde (silver catalyst).

All air oxidation processes use a combination of absorption devices, condensers, or carbon adsorption units for product recovery (or for recovery of unreacted raw material). These devices are usually designed to recover only as much of the VOC as is economically feasible and therefore would not be considered control devices. However, in some plants, these devices are designed to remove more than that amount which is economically justified. In this case, the devices operate both for product recovery and as control devices for emission reduction or to reduce the pollutant load on some other final control device.

Table 4-1 shows some of the SOCMI air oxidation chemical processes and the product recovery-VOC emission control methods used.

4.2 ADSORPTION

The main function of vapor-phase carbon adsorption is to contain and concentrate dilute organic vapors from waste streams where condensers or absorbers are ineffective or uneconomical. Carbon adsorption in most cases is used for recovery of expensive, unreacted raw material and not for VOC emission control. The major application of carbon adsorption in air oxidation processes is for the recovery of aromatic feedstocks such as benzene, xylene, and cumene. Selected air oxidation processes known to employ carbon adsorption are listed in Table 4-2.

TABLE 4-1. PRODUCT RECOVERY AND EMISSION CONTROLS CURRENTLY USED IN ONE OR MORE PLANTS EMPLOYING MAJOR AIR OXIDATION PROCESSES

Chemical	Process	Product or Raw Material Recovery Equipment	Emission Control Equipment
Acetaldehyde	Wacker	1, 2	
Acetic Acid	Wacker	1, 2	
Acetic Acid/Formic Acid/Methyl Ethyl Ketone	Butane	1, 2	
Acetone/Phenol	Cumene Peroxidation	1, 3	
Acrylonitrile	Propene Ammoxidation	1, 2	5, 6
Acrylic Acid	Propene	1, 2	4B
1,3-Butadiene	Butene Oxidative Dehydrogenation	1, 2	4B
Cyclohexanol/Cyclohexanone	Cyclohexane	1, 2	
Ethylene Dichloride	Ethylene Oxychlorination	1, 2	4B, 5
Ethylene Oxide	Ethylene	1, 2	5
Formaldehyde	Silver Catalyst	1, 2	6
Formaldehyde	Mixed Metal Oxide Catalyst	1, 2	
Hydrogen Cyanide	Andrussow	2	6
Maleic Anhydride	Benzene	1, 2, 3	4B, 5, 6
Maleic Anhydride	Butane	1, 2	4
Phthalic Anhydride	Naphthalene	1, 2	4
Phthalic Anhydride	Xylene	1, 2	4B
Propylene Oxide/Styrene	Ethylbenzene Peroxidation	1, 2	
Terephthalic Acid/Dimethyl Terephthalate	Xylene	1, 2, 3	

KEY:

1	Condenser
2	Absorber
3	Carbon Adsorber
4	Thermal Incinerator
4B	Thermal Incinerator - Waste Heat Boiler
5	Catalytic Incinerator
6	Process Heater or Boiler

TABLE 4-2. SELECTED AIR OXIDATION PROCESSES KNOWN TO USE CARBON ADSORPTION FOR PRODUCT/RAW MATERIAL RECOVERY OR EMISSION REDUCTION

Chemical	Primary Compound Recovered
Acetone/Phenol	Cumene
Maleic Anhydride	Benzene
Terephthalic Acid/ Dimethyl Terephthalate	Xylene

Adsorption devices work by capturing vapor-phase molecules upon the surface of a solid. The molecules adhere primarily through two mechanisms: (1) physical adsorption, in which Van der Waal's forces attract and hold the gas molecules to the adsorbent surface, and (2) chemical adsorption (chemisorption), in which the molecules are chemically bonded to the adsorbent.[1]

Oxygenated adsorbents such as silica gels, fullers, diatomaceous, and other siliceous earths, synthetic zeolites, and metallic oxides exhibit greater selectivity than activated carbon. However, due to their affinity for polar molecules, they have a greater preference for water than organics and are of little use on the moist air streams from SOCMI air oxidation process vents.[2] Vent stream dehumidification may be possible but will necessitate more equipment and increase treatment cost.

4.2.1 Carbon Adsorption Process

Material recovery by carbon adsorption may be too difficult or expensive for some chemicals when their vapor concentrations are below 700 ppmv.[3] Although carbon adsorption system configurations vary according to the volume of gas handled and allowable pressure drop, a typical set-up is shown in Figure 4-1. After filtering and cooling, the waste gas is directed through a bed of carbon granules (Adsorber 1). In time, traces of organic vapors appear in the exit air and the removal efficiency rapidly decreases (breakthrough). At this point, the waste gas stream is routed through a fresh bed, and the saturated bed is regenerated by passing a hot gas through it to desorb (strip) the organics from the carbon. Low-pressure steam is a common regeneration fluid providing a concentration gradient to facilitate mass transfer of adsorbate from the carbon bed and supplying the heat of desorption. The steam and organic vapors are then condensed and the organics separated from the water by decantation and/or distillation. The freshly-regenerated bed is cooled, dried, and prepared for another service cycle.

4.2.2 Carbon Adsorption Emissions Removal Efficiency

State-of-the-art carbon adsorption systems for VOC recovery can have outlet concentrations in the range of 50 to 100 ppmv with concentrations as low as 10 to 20 ppmv achievable with some compounds.[4] For inlet concentrations

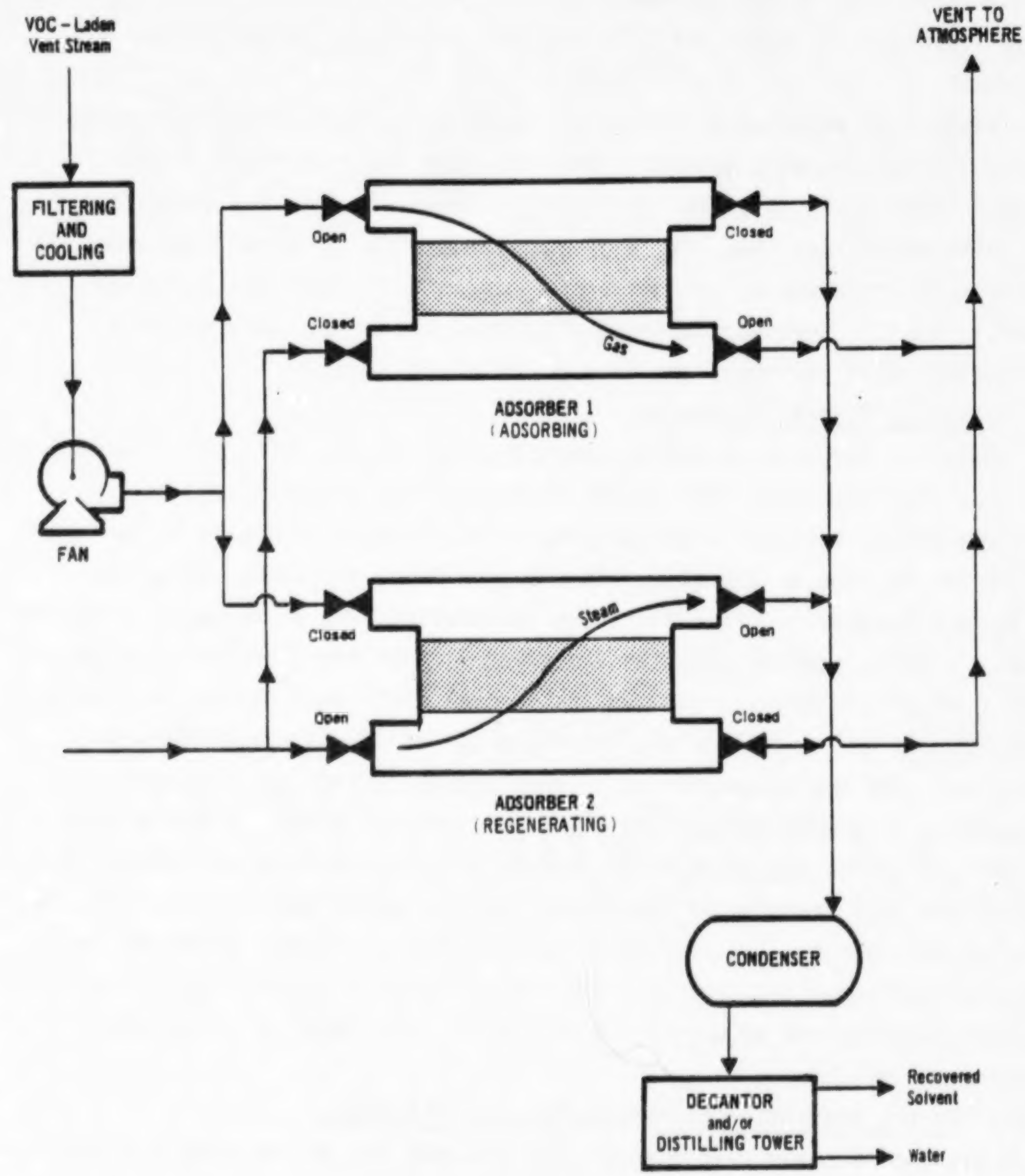
VOC - Laden Vent Stream
FILTERING AND COOLING
FAN
VENT TO ATMOSPHERE
Open
Closed
Closed
Open
Gas
ADSORBER 1 (ADSORBING)
Closed
Open
Steam
Open
Closed
ADSORBER 2 (REGENERATING)
CONDENSER
DECANTOR and/or DISTILLING TOWER
Recovered Solvent
Water

Figure 4-1. Two stage regenerative adsorption system.

from 700 to 5000 ppmv, these numbers yield an expected VOC adsorption removal efficiency range of 86 to 99 percent. Adsorption removal efficiencies up to 95 percent can be achieved from some chemicals in well-designed systems.[5]

4.2.3 Parameters Affecting VOC Removal Efficiency

The most important operating parameter affecting continuing VOC removal efficiency is the amount of steam used for regeneration. The graph given as Figure 4-2 shows a generalized form of the relationship of effluent VOC concentration to steam usage. The exact relationship depends on the type of VOC being removed and on the operating characteristics of the system. Figure 4-2 shows that reduced effluent concentration is obtained by increasing the steam ratio and that very low effluent concentration levels may be obtained with high steam ratio. Figure 4-2 shows that the position of the effluent concentration curve for each particular compound is a function of the adsorption temperature, regeneration temperature, and carbon loading capacity. The effluent concentration curve is relatively independent of inlet VOC concentrations. When the adsorption temperature increases, the effluent concentration curve baseline may increase. Higher regeneration temperatures may shift the effluent outlet concentration curve downward. A different loading capacity may shift the curve laterally, since different amounts of steam may be required to regenerate the carbon.[6]

VOC with molecular weights below 45 do not adsorb well on carbon; high (>130) molecular weight VOC are more difficult to remove during regeneration.[7] Also, during adsorption of multicomponent gas streams, the higher boiling point components tend to displace the lower boiling point components from the adsorption sites on the carbon.[8]

Adsorption rates decrease sharply for gas streams with temperatures of 38°C (100°F) and above.[9,10] Inlet VOC concentrations may be limited to 25 percent of LEL (~5000 ppmv) by insurance requirements. Although some moisture is desirable in the waste gas to provide more uniform bed temperatures, excessive humidity can adversely affect the VOC removal efficiency of a carbon adsorption system. Mist in the gas stream can rapidly saturate an adsorption bed, taking up adsorption sites. Operating capacity decreases become pronounced at relative humidities over 50 percent.[11]

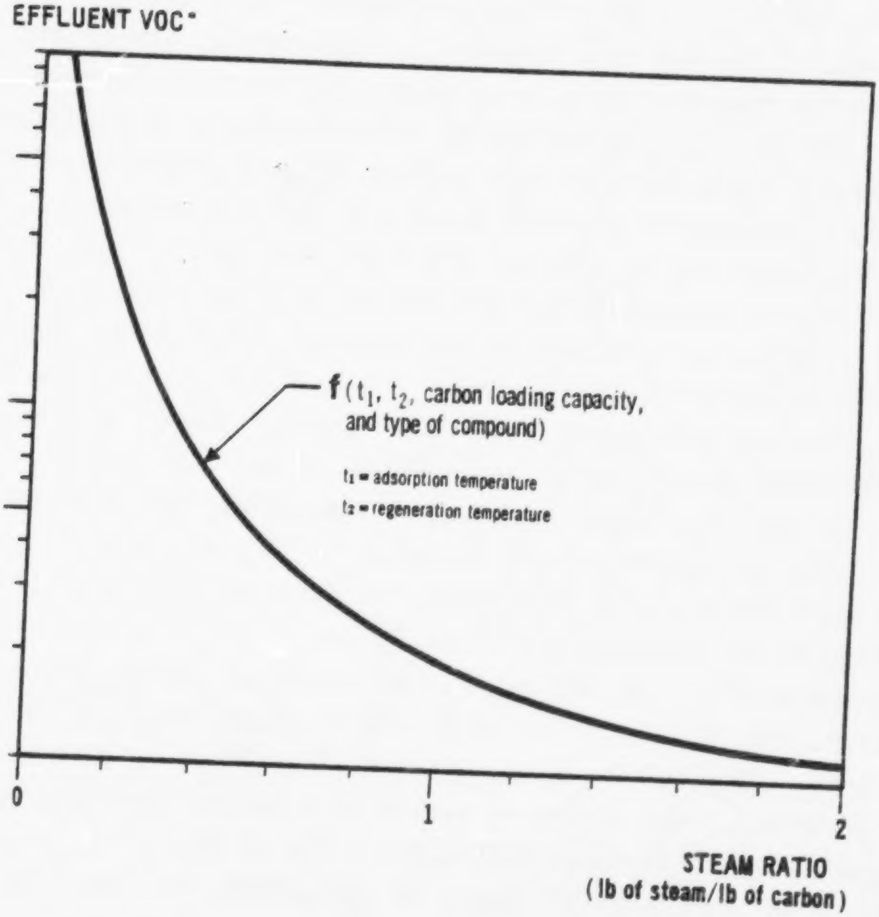

Figure 4-2. Generalized form of the relationship of effluent VOC concentratiion to steam usage.

4.2.4 Factors Affecting Applicability and Reliability

Although carbon adsorption can be used for product recovery and to help control VOC emissions, it is not a control method generally applicable to SOCMI air oxidation processes. The vent streams from some of these processes are often saturated with moisture. This would result in serious loss of adsorption capacity due to the water saturating the adsorbing medium and taking up adsorption sites. Such process vent streams require dehumidification to lower the water content. Process upsets which increase vent stream VOC composition are not uncommon in air oxidation processes, and may result in an excessive temperature rise due to the accumulated heat of adsorption of the extra VOC loading.

4.3 ABSORPTION

Absorption is one of the two primary methods of product recovery used in air oxidation processes. Absorbers are also commonly applied as auxiliary control devices prior to combustion devices. An absorber can be added to an existing process for the purpose of VOC control, or an existing absorber could be modified, perhaps by an increase in the size or a decrease in the operating temperature, for the purpose of VOC control. Some of the air oxidation processes which employ absorption are listed in Table 4-3.

Gas absorption devices work by dissolving the soluble components of a gaseous mixture in a liquid. Absorption may only entail the physical phenomenon of solution or may also involve chemical reaction of the solute with constituents of the solution.[12] The absorbing liquids (solvents) used are chosen for high solute (VOC) solubility and include liquids such as water, mineral oils, non-volatile hydrocarbon oils, and aqueous solutions of acid-neutralizing agents like sodium carbonate and sodium hydroxide.[13] Devices based on absorption principles include spray towers, venturi scrubbers, packed columns, and plate columns. Spray towers require high pressure to obtain droplets ranging in size from 500 to 1000 μm in order to present a sufficiently large surface contact area.[14] They can remove particulate matter without plugging, but have the least effective mass transfer capability and thus, are restricted to particulate removal and control of high-solubility gases such as sulfur dioxide and ammonia.[15] Venturi scrubbers have a high degree of gas-liquid mixing and high particulate removal efficiency but

TABLE 4-3. SELECTED AIR OXIDATION PROCESSES KNOWN TO USE ABSORPTION FOR PRODUCT RAW MATERIAL RECOVERY OR EMISSIONS REDUCTION

Chemical
Acetaldehyde
Acetic Acid/Formic Acid/MEK
Acrylonitrile
Acrylic Acid
1,3-Butadiene
Cyclohexanol/Cyclohexanone
Ethylene Dichloride
Ethylene Oxide
Formaldehyde
Hydrogen Cyanide
Maleic Anhydride
Phthalic Anhydride
Propylene Oxide/Styrene
Terephthalic Acid/Dimethyl Terephthalate

require high pressure and have relatively short contact times, so their use is also restricted to high-solubility gases.[16] The choice for gas absorption is thus between packed and plate columns. Packed columns are mostly used for handling corrosive materials and liquids with foaming or plugging tendencies. They are less expensive than plate columns for small-scale or pilot plant operations where the column diameter is less than 0.6 m (2 ft). Plate columns are preferable for large-scale operations, where internal cooling is desired and where low liquid flowrates would inadequately wet the packing.[17]

4.3.1 Absorption Process

The mechanism of absorption consists of the selective transfer of one or more components of a gas mixture into a solvent liquid. The transfer consists of diffusion to the solvent and dissolution into it. For any given solvent, solute, and set of operating conditions, there exists an equilibrium ratio of solute concentration in the gas mixture to concentration in the solvent. The driving force for mass transfer at a given point in the operating tower is related to the difference between the actual concentration ratio and the equilibrium ratio.[19]

A schematic of a packed, gas absorption tower is shown in Figure 4-3. The waste gas containing VOC enters at the bottom and rises through the packing, contacting the absorbing liquid on the surface of the packing material. The VOC (solute) is dissolved in the absorbent liquid (solvent) and is discharged at the bottom of the tower for recovery or disposal. The cleaned gas exits at the top with reduced VOC concentration, ready for release or final treatment such as incineration.

4.3.2 Absorption VOC Removal Efficiencies

Systems that utilize organic liquids as solvents usually include the stripping and recycle of the solvent to the absorber. In this case the VOC removal efficiency of the absorber is dependent on the solvent stripping efficiency. If, for example, a system achieved a removal efficiency in excess of 99 percent with once-through solvent usage, it would be expected that the removal efficiency would drop to about 94 percent with solvent recycling.[20] Once-through solvent usage can create a liquid waste problem and incur additional treatment costs.

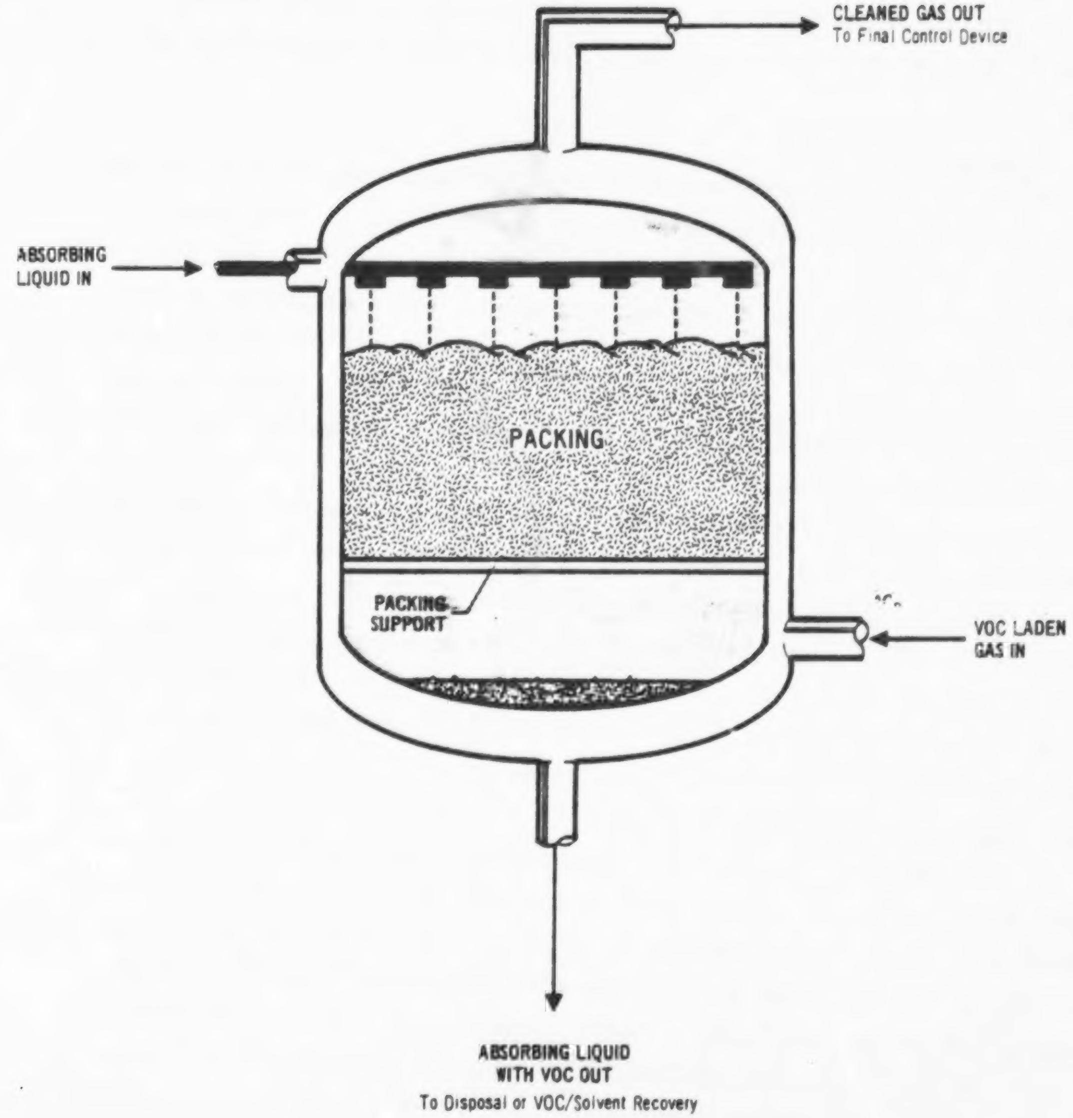
CLEANED GAS OUT
To Final Control Device
ABSORBING LIQUID IN
PACKING
PACKING SUPPORT
VOC LADEN GAS IN
ABSORBING LIQUID WITH VOC OUT
To Disposal or VOC/Solvent Recovery

Figure 4-3. Packed tower for gas absorption.

For a given absorbent and absorbate, an increase in absorber size or a decrease in the operating temperature can increase the VOC removal efficiency of the system. It may be possible in some cases to increase VOC removal efficiency by a change in the absorbent.

4.3.3 Factors Affecting Efficiency and Reliability

The effectiveness of an absorption tower, which is the rate of mass transfer between the two phases, is largely dependent upon the available gas-liquid contact area. In packed towers, a reduction in the liquid-to-gas ratio can lead to channeling where some of the packing is not wetted by the liquid. Excessive gas flowrates can increase the liquid holdup until the tower floods and liquid exits at the top with the gas.

VOC concentration can affect the operation of absorption equipment. Excessive VOC loading can raise the temperature of the tower due to increased rate of release of the heat of solution, resulting in a decreased concentration gradient. Absorption is usually not considered when the VOC concentration is below 200-300 ppmv.[21]

4.4 CONDENSATION

Condensation is one of the two primary methods of product recovery used in air oxidation processes. Condensers are also commonly applied as auxiliary control devices before thermal incinerators, adsorbers, and other control devices.[22] An existing condenser can be modified for improved VOC emission control by lowering the operating temperature. The suitability of condensation as an emissions control method depends on several parameters. These include the VOC concentration at the inlet (usually >1 percent), the VOC removal efficiency required, the VOC recovery value, and the size of the condenser required for handling the gas volume flowrate.[23] Air oxidation processes which employ condensation are listed in Table 4-4.[24]

Condensation devices are usually surface or contact condensers.[25] Contact condensers spray a cooled liquid directly into the gas stream, also acting as scrubbers in removing normally noncondensable vapors.[26] The coolant is usually water or perhaps a process feed stream.[27] Contact condensers are generally cheaper, more flexible and efficient for VOC removal. However, the spent coolant can present a secondary emissions

TABLE 4-4. SELECTED AIR OXIDATION PROCESSES KNOWN TO USE CONDENSATION FOR PRODUCT RAW MATERIAL RECOVERY OR EMISSIONS REDUCTION

Chemical
Acetaldehyde
Acetic Acid/Formic Acid/MEK
Acetone/Phenol
Acrylonitrile
Acrylic Acid
1,3-Butadiene
Cyclohexanol/Cyclohexanone
Ethylene Dichloride
Ethylene Oxide
Formaldehyde
Maleic Anhydride
Phthalic Anhydride
Propylene Oxide/Styrene
Terephthalic Acid/Dimethyl Terephthalate

source or waste water treatment problem.[28] Surface condensers have more auxiliary equipment but can recover valuable and marketable VOC. They do not contaminate the coolant, therefore minimizing waste disposal problems. Only surface condensers are discussed in this section.

4.4.1 Condensation Process

Condensation occurs when the partial pressure of a condensable component equals its vapor pressure at that temperature. Most surface condensers are of the shell-and-tube type and achieve condensation by removing heat from vapors.[29] As the coolant passes over the tubes, the VOC vapors condense inside the tubes and are recovered. The coolant used depends upon the saturation temperature (dewpoint) of the VOC. Chilled water can be used down to 7^oC (45^oF), brines to -34^oC (-30^oF), and chlorofluorocarbons below -34^oC (-30^oF).[30] Temperatures as low as -62^oC (-80^oF) may be necessary to obtain the required VOC removal efficiencies.[31] A table of the estimated operating temperature required to achieve a given VOC removal efficiency is given in Reference 31. These temperatures were estimated for aliphatic and halogenated aliphatic hydrocarbons as a function of inlet VOC concentration.

The major pieces of equipment of a condenser system (as shown in Figure 4-4) are the shell-and-tube heat exchanger (condenser), refrigeration system (coolant supply), storage tanks, and pumps.

4.4.2 Condenser VOC Removal Efficiency

VOC removal efficiencies of 50 percent are typical of a condenser used in conjunction with other control devices. The maximum efficiency reported is close to 95 percent with average efficiencies of 80 percent reported in the literature.[32]

4.4.3 Parameters Affecting Reliability and Efficiency

Condensers used for VOC control often operate at temperatures below the freezing point of water. This requires that moist vent streams, such as those found in air oxidation processes, be dehumidified before VOC removal to prevent the formation of ice in the condenser. Particulate matter must not be allowed to enter a surface condenser system since it may deposit on the finned tubes and interfere with gas flows and heat transfer. Gas flowrates from 100 to 2000 cfm are representative of the capacity range for condensers as emission control devices. Vent streams containing less than one-half percent VOC are generally not considered for control by condensation.[33]

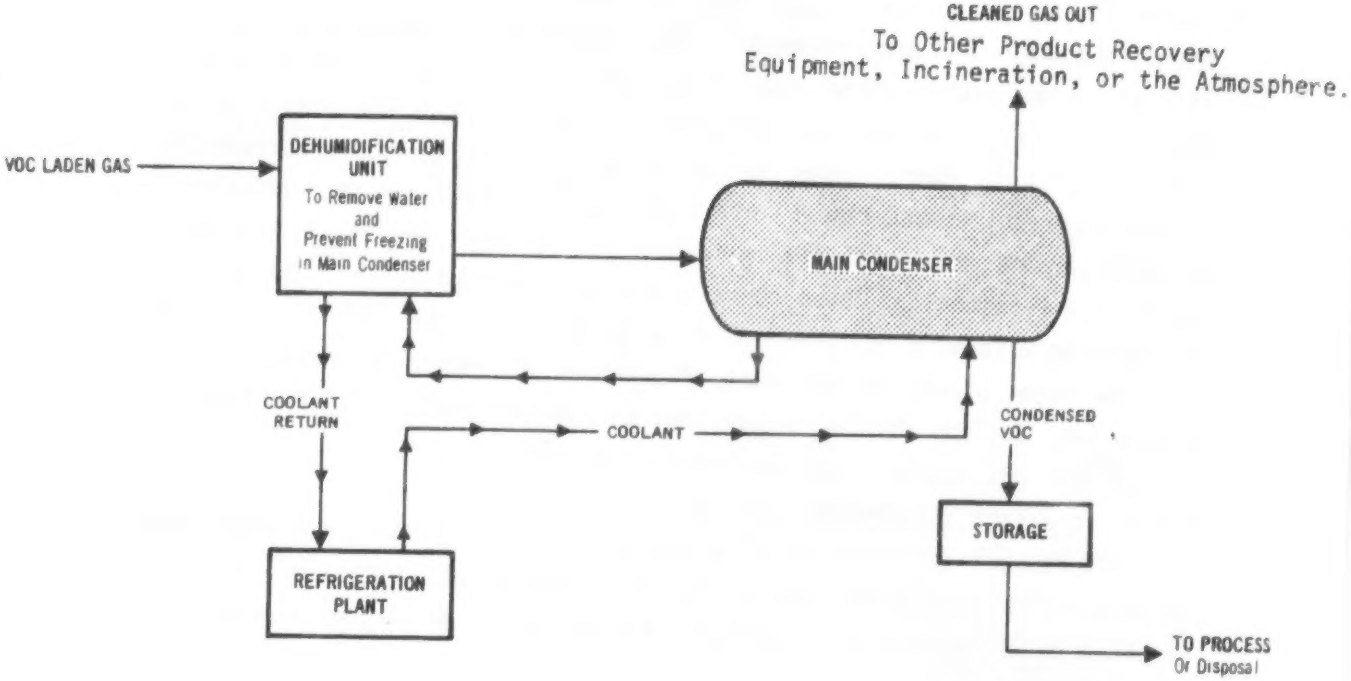
CLEANED GAS OUT
To Other Product Recovery Equipment, Incineration, or the Atmosphere.
VOC LADEN GAS
DEHUMIDIFICATION UNIT
To Remove Water and Prevent Freezing in Main Condenser
MAIN CONDENSER
COOLANT RETURN
COOLANT
CONDENSED VOC
STORAGE
REFRIGERATION PLANT
TO PROCESS
Or Disposal

Figure 4-4. Condensation system.

4.5 CONTROL BY COMBUSTION TECHNIQUES

Combustion control techniques result in the destruction of the raw material or product present in the offgas. Therefore, they are usually to be considered add-on emission control techniques. Although the process material can never be recovered, it is possible to recover much of the thermal energy released by combustion. In the case of offgas with a high heating value, it may be economically attractive to combust the vent stream in a boiler or process heater.

4.5.1 General Combustion Principles

Combustion is a rapid, exothermic oxidation process which results in the complete or incomplete oxidation of VOC. Most fuels and VOC contain carbon and hydrogen which, when burned to completion with oxygen, form carbon dioxide and water.

Since air oxidation vent streams generally contain little oxygen, additional combustion air must be provided. The total gas volume flow is therefore relatively larger than that associated with other types of control.

4.5.2 Combustion Control Devices

Control devices using combustion principles include furnaces, boilers, and thermal and catalytic oxidizers. Combustion in thermal and catalytic oxidizers are the usual control methods for air oxidation processes.

Furnaces and boilers are only occasionally used as control devices for the larger air oxidation vent streams because the fuel requirements of their firing cycles may not coincide with the availability or heating value of the offgas. Waste streams with large flows and low heating values can adversely affect the operation of these devices in two ways. By lowering furnace temperatures, they cause incomplete combustion and diminished steam production. Furthermore, an increased volume flow of gases can exceed the handling capabilities of the exhaust system.

Catalytic oxidizers are not widely used because the catalysts can be poisoned by sulfur- and halogen-containing compounds. Moreover, increases of VOC concentration in poorly controlled streams can raise the catalyst bed temperature excessively to the point of deactivating the catalyst.

4.5.3 Thermal Oxidizers

Thermal oxidation is the method of VOC emission control most widely used for air oxidation processes because it is applicable to a variety of chemicals and vent streams conditions. Incineration is the usual method of pollution control for waste streams with combustible concentration below the LEL (about 470 $\frac{\text{kcal}}{\text{Nm}^3}$ or 53 $\frac{\text{Btu}}{\text{scf}}$) such as those found in SOCMI air oxidation processes.[34] Table 4-5 is a partial listing of chemical processes using thermal oxidation for VOC control.

Thermal oxidizers can also control halogenated VOC. However, a higher chamber temperature is required to properly oxidize chlorinated hydrocarbons and convert the noxious combustion products to a form more readily removable by flue gas scrubbing.

4.5.3.1 Thermal Oxidation Process

The combustion process is influenced by time, mixing, and temperature. An efficient thermal oxidizer must provide:

1. A chamber temperature high enough to enable the oxidation reaction to proceed rapidly to completion,
2. Enough turbulence to obtain good mixing between the hot combustion products from the burner, combustion air, and VOC, and
3. Sufficient residence time at the chosen temperature for the oxidation reaction to reach completion.

Combustion chamber temperature is an important parameter in the design of a thermal oxidizer since oxidation rates are highly temperature-dependent. Incineration of low heating value offgas necessitates the burning of an auxiliary fuel to achieve the desired chamber temperature. As discussed in Appendix C, destruction of most VOC occurs rapidly at temperatures over 760°C (1400°F). However, higher temperatures, on the order of 980°-1100°C (1800°-2000°F), may be required when incinerating halogenated VOC.

Mixing is crucial in achieving good thermal oxidizer performance. A properly designed incinerator rapidly combines the offgas, combustion air, and hot combustion products from the burner. This ensures that the VOC be in contact with sufficient oxygen at a temperature high enough to start the oxidation reaction. Improper mixing can permit packets of waste gas to pass through the incinerator intact. Poor mixing can also lead to poor temperature distributions so that not all the waste gas stream reaches or remains at the design combustion temperature.

TABLE 4-5. PARTIAL LIST OF AIR OXIDATION CHEMICALS USING THERMAL OXIDIZER FOR CONTROLLING VOC EMISSIONS FROM OFFGAS STREAM

Chemical	Number of Plants Reported	Reported Operating Temperature (°F)	Reported Efficiency
Butadiene	1[a]	Not Reported	Not Reported
Acrylic Acid	3[b]	Not Reported	Not Reported
Acrylonitrile	2[c]	1800	>99%[c]
Formaldehyde	4[d]	2000	99.8-100%[d]
Phthalic Anhydride	1[e]	1200	90-95%
Maleic Anhydride	3[f]	1400	93%
Maleic Anhydride	3[f]	1600	99%

[a] Standifer, R.L. Draft Butadiene Abbreviated Product Report. Hydroscience. EPA Contract No. 68-02-2577.

[b] Blackburn, J.W. Draft Acrylic Acid and Ester Product Report. Hydroscience. EPA Contract No. 68-02-2577.

[c] Hobbs, F.D. and Key, J.A. Draft Acrylonitrile Product Report. Hydroscience. EPA Contract No. 68-02-2577.

[d] Lovell, R.J. Draft Formaldehyde Product Report. Hydroscience. EPA Contract No. 68-02-2577.

[e] Office of Air and Waste Management. U.S. Environmental Protection Agency. Research Triangle Park, NC. Control Techniques for Volatile Organic Emissions from Stationary Sources. Publication No. EPA-450/2-78-022. May 1978.

[f] Lawson, J.F. Draft Maleic Anhydride Product Report. Hydroscience. EPA Contract No. 68-02-2577.

Residence time is the time available for the oxidation reaction to occur within the combustion chamber. Residence times from as low as 0.3 to several seconds have been used in thermal oxidizer design.[35] Vendors generally define residence times in one of two ways. Some count offgas residence time in any of the available volume of the combustion chamber. Others credit only residence time within that volume in which the flue gas is at the combustion temperature. It is this volume which is theoretically related to destruction efficiency. Therefore, incinerator efficiency data which use the latter definition of residence time are more easily compared in an analysis of the relationship of destruction efficiency to residence time. Moreover, according to this definition, a larger combustion chamber is required to achieve a given residence time. Therefore, this definition yields more conservative (higher) estimates of the cost of control.

Other parameters affecting oxidizer performance are offgas heating value, water content, and excess combustion air. The offgas heating value is a measure of the heat available from the combustion of the VOC in the offgas to CO_2 and H_2O. The heat of combustion for specific organic compounds can range from 950 $\frac{KJ}{scm}$ (25 $\frac{Btu}{scf}$) for carbon tetrachloride (CCl_4) to 35,700 $\frac{KJ}{scm}$ (960 $\frac{Btu}{scf}$) for methane (CH_4).[36] Incineration of offgas with a low heating value (less than 1860 $\frac{KJ}{scm}$ (50 $\frac{Btu}{scf}$)) may require the burning of an auxiliary fuel to maintain the desired combustion temperature. Auxiliary fuel requirements can be lessened or eliminated by the use of recuperative heat exchangers. Offgas with a heating value above 1860 $\frac{KJ}{scm}$ (50 $\frac{Btu}{scf}$) may support combustion but may need auxiliary fuel for flame stability. Combustion of an offgas with a heating value over 5200 $\frac{KJ}{scm}$ (140 $\frac{Btu}{scf}$) can result in flame temperatures in excess of 1200°C (2200°F). Conventional oxidation equipment can only be used for such streams if the temperature is kept below 1200°C (2200°F) by addition of air, water vapor, or liquid water, or circulation of exhaust gas. If boilers are used, dilution of the streams would not be necessary.

A thermal oxidizer handling offgas streams with varying heating values requires adjustment to maintain the proper chamber temperatures and operating efficiency. Water has a heat of vaporization of

$41{,}390 \frac{\text{KJ}}{\text{kg mol}}$ $(18{,}000 \frac{\text{Btu}}{\text{lb mol}})$ and a heat capacity of about $27.5 \frac{\text{KJ}}{\text{kg mol }^{\circ}\text{C}}$ $(11.8 \frac{\text{Btu}}{\text{lb mol }^{\circ}\text{F}})$ at 870°C (1600°F) and 101 kPa (14.7 psia).[37] Entrained water droplets in an offgas stream can substantially increase auxiliary fuel requirements due to the additional energy needed to vaporize the water and raise it to the combustion chamber temperature. Combustion devices are operated with some quantity of excess air to ensure a sufficient supply of oxygen. Too much excess air causes an increase in auxiliary fuel requirements since the extra air is heated up to chamber temperature. Too much excess air also increases the thermal oxidizer's flue gas volume flow rate and, thus, its size and cost.

4.5.3.2 Thermal Oxidizer Design

A thermal oxidizer is usually a refractory-lined chamber containing a burner at one end and generally operated at a temperature of 550°-850°C with a residence time of from 0.3 to one second.[38]

Discrete dual fuel burner(s) and inlets for the offgas and combustion air are so arranged in the chamber to thoroughly mix the hot products from the burners with the offgas and air streams. The mixture of hot reacting gases then passes into the reaction section. This section is sized to allow the mixture enough time at the elevated temperature for the oxidation reaction to reach completion. Energy can then be recovered from the hot flue gases in the heat recovery section. Preheating of combustion air or offgas are common modes of energy recovery; however, it is sometimes more economical to generate steam. Insurance regulations require that if the waste stream is preheated, the VOC concentration be maintained below 25 percent of LEL to eliminate explosion hazards.

Thermal oxidizers designed specifically for VOC incineration with natural gas as the auxiliary fuel may use a grid-type (distributed) gas burner instead of the conventional dual fuel, forward flame, discrete burners. The tiny gas flame jets on the grid surface ignite the vapors as they pass through the grid and ensure burning of all the vapors at lower chamber temperatures using less fuel and allowing for a shorter reaction chamber.[39] Typical configurations are shown in Figures 4-5 and 4-6.

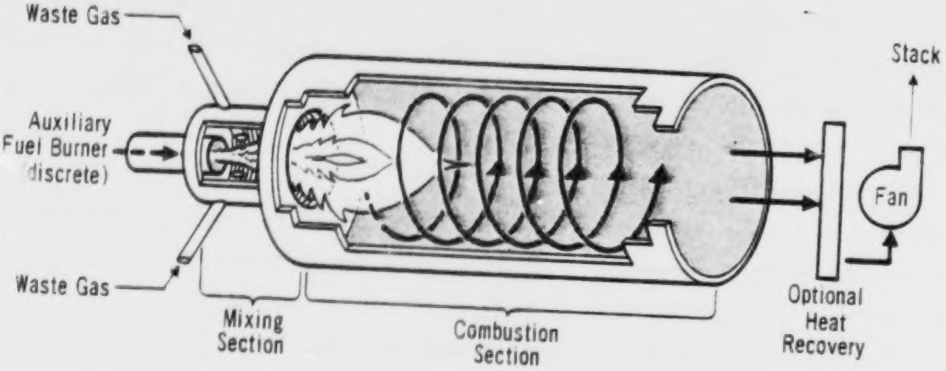
Waste Gas
Auxiliary Fuel Burner (discrete)
Waste Gas
Mixing Section
Combustion Section
Optional Heat Recovery
Fan
Stack

Figure 4-5. Discrete burner, thermal oxidizer.

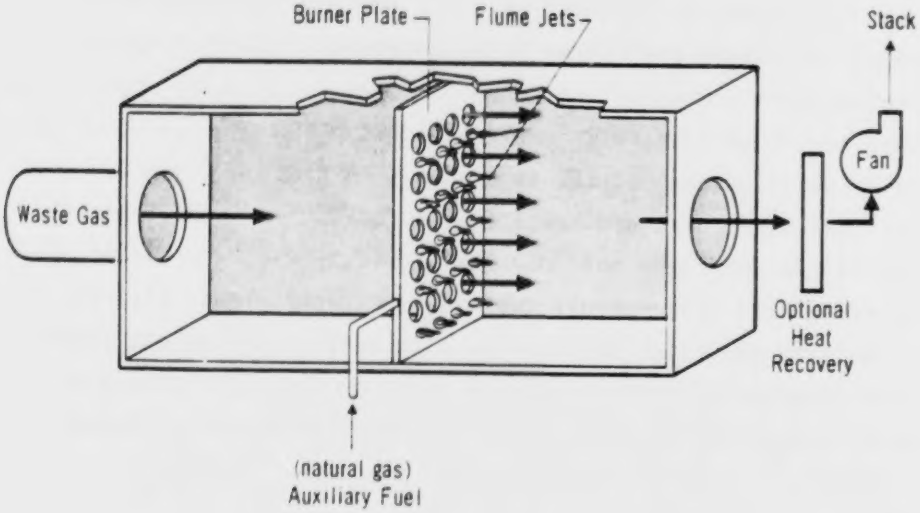
Burner Plate
Flume Jets
Stack
Fan
Waste Gas
Optional Heat Recovery
(natural gas) Auxiliary Fuel

Figure 4-6. Distributed burner, thermal oxidizer.

Thermal oxidizers for chlorinated VOC control require additional control equipment. The flue gases are quenched to lower their temperature and routed through absorption equipment such as towers or liquid jet scrubbers to remove the noxious combustion products. A waste-heat boiler, constructed of a corrosion resistant alloy, is employed for heat recovery.

Packaged, single unit thermal oxidizers can be built to control streams with flowrates in the range of a few hundred scfm to about 50,000 scfm. A typical thermal oxidizer built to handle a VOC waste stream of 850 $\frac{\text{scm}}{\text{min}}$ (30,000 scfm) at a temperature of 870°C (1600°F) with 0.75 second residence time probably would be a refractory-lined cylinder. As discussed in Chapter 8, a typical ratio of flue gas to waste gas is about 2.2, (both flowrates at standard temperature). The chamber volume necessary to provide the residence time at that temperature would be about 99 m^3 (3500 ft^3). If the chamber length to diameter ratio is two to one, a typical design, and allowing a 30.5 cm (1 ft) wall thickness, the thermal oxidizer would measure 8.3 m (27 ft) long by 4.6 m (15 ft) wide, exclusive of heat exchangers and exhaust equipment.

4.5.3.3 Thermal Oxidizer Emission Destruction Effectiveness

Based on a study of thermal oxidizer efficiency, cost and fuel use, it is concluded that 98 percent VOC reduction, or 20 ppmv as compound exit concentration (whichever is less stringent) is the highest reasonable control level achievable by all new incinerators in all air oxidation processes, considering current technology.[40] An analysis assuming achievement of this efficiency with incinerator operation at 870°C (1600°F) and 0.75 second residence time yields conservative estimates of costs and energy use.

The VOC destruction efficiency of an incinerator can be affected by variations in chamber temperature, residence time, inlet concentration, compound type, and flow regime (mixing). A combustion chamber temperature of 870°C (1600°F) was chosen for the analysis on the basis that higher temperatures, with higher control efficiencies, are preferred. Test results show that 98 percent destruction efficiency is achievable at various temperatures (700°C (1300°F) to 800°C (1500°F)) and residence times (0.5 to 1.5 seconds).[41] Kinetics calculations comparing the test conditions to 870°C (1600°F) temperature with 0.75 second residence time show that the latter set of conditions is more conducive to complete VOC destruction. Cost per pound of VOC controlled increases only 5 to 10 percent with an increase in temperature from 760°C (1400°F) to 870°C (1600°F) with the use of 70 percent recuperative heat recovery. Temperature higher than 870°C (1600°F) were not used in this analysis due to the materials limitations of metallic heat exchangers. Higher temperatures would require heat exchange surfaces to be made of more expensive materials.

Variations in inlet concentration can change a thermal oxidizer's VOC destruction efficiency. Kinetics calculations describing the complex combustion reaction mechanisms point to much slower reaction rates at very low compound concentrations. Available data show that 20 ppmv as compound maximum outlet concentration is a reasonable limit which allows for the drop in achievable destruction efficiency with decreasing inlet concentration.[42]

The data also show that the variation of destruction efficiency as a function of compound identity is greater at temperatures lower than 760°C (1400°F), although precise quantitative relations could not be determined. The types of compounds in the data include C_1 to C_5 alkanes and olefins, aromatics such as benzene, toluene, and xylene and oxygenated compounds such as MEK and isopropanol. Nitrogen-containing species such as acrylonitrile and ethylamines and chlorinated compounds such as vinyl chloride are also included in the data.

At temperatures over 760°C (1400°F), the oxidation reaction rate is much faster than the rate at which mixing takes place. Therefore, VOC destruction becomes more dependent upon the fluid mechanics within the oxidation chamber. The flow regime should be such that the mixing of the VOC stream, combustion air, and hot combustion products from the burner be rapid and thorough. This enables the VOC to attain the combustion temperature in the presence of enough oxygen for a sufficient period of time for the oxidation reaction to reach completion. Chamber design and burner and baffle configurations provide for turbulent flow for improved mixing. As discussed in Appendix C, the most practical manner of achieving good mixing and efficiency is to adjust the installed equipment to improve performance.

Thermal oxidation at a control efficiency lower than 98 percent was not considered as an alternative control technique. VOC control by combustion at efficiencies of 90 percent or less would result in an adverse environmental impact. This impact would result because the remaining 10 percent of VOC emissions would consist of noxious, partially oxidized organic compounds (particularly for halogenated vent streams).[43]

4.5.4 Catalytic Oxidizers

Catalytic oxidation is the second major combustion technique for VOC emissions control. Selected air oxidation processes known to use catalytic oxidation for emission control are listed in Table 4-6.

A catalyst works by changing the rate of a chemical reaction without becoming permanently altered itself. Catalysts for catalytic oxidation cause a higher rate of reaction at a lower energy level (temperature), allowing oxidation of VOC at lower temperatures than for thermal oxidation. Combustion catalysts include platinum and platinum alloys, copper oxide, chromium and cobalt.[44] These are deposited in thin layers on inert substrates to provide for maximum surface contact area.

For certain processes, catalytic oxidation under pressure is employed as an essential element in highly integrated air compression/energy recovery cycles. In such applications, it is not a terminal control device (although it is an efficient destruction device) and, therefore, cannot lend itself well to replacement or supplementation.

4.5.4.1 Catalytic Oxidation Process

In catalytic oxidation, a waste oxidation, a waste stream and air are contacted with a catalyst at a temperature sufficiently high to allow the oxidation reaction to occur. The waste gas is introduced into a mixing chamber where it is heated to the proper temperature (about 316°C (600°F)) by contact with the hot combustion products of a burner. The heated mixture is then passed through the catalyst bed as shown in Figure 4-7. VOC and oxygen are transferred to the catalyst surface by diffusion from the waste gas and chemisorbed in the pores of the catalyst to the active sites where the oxidation reaction takes place. The reaction products are then desorbed from the active sites and transferred by diffusion back into the waste gas.[44] The cleaned gas may then be passed through a waste heat recovery device before exhausting into the atmosphere.

TABLE 4-6. SELECTED AIR OXIDATION PROCESSES KNOWN TO USE CATALYTIC OXIDATION FOR EMISSION CONTROL

Chemical
Acrylonitrile
Ethylene Dichloride
Ethylene Oxide
Maleic Anhydride
Formaldehyde (Mixed Oxide)

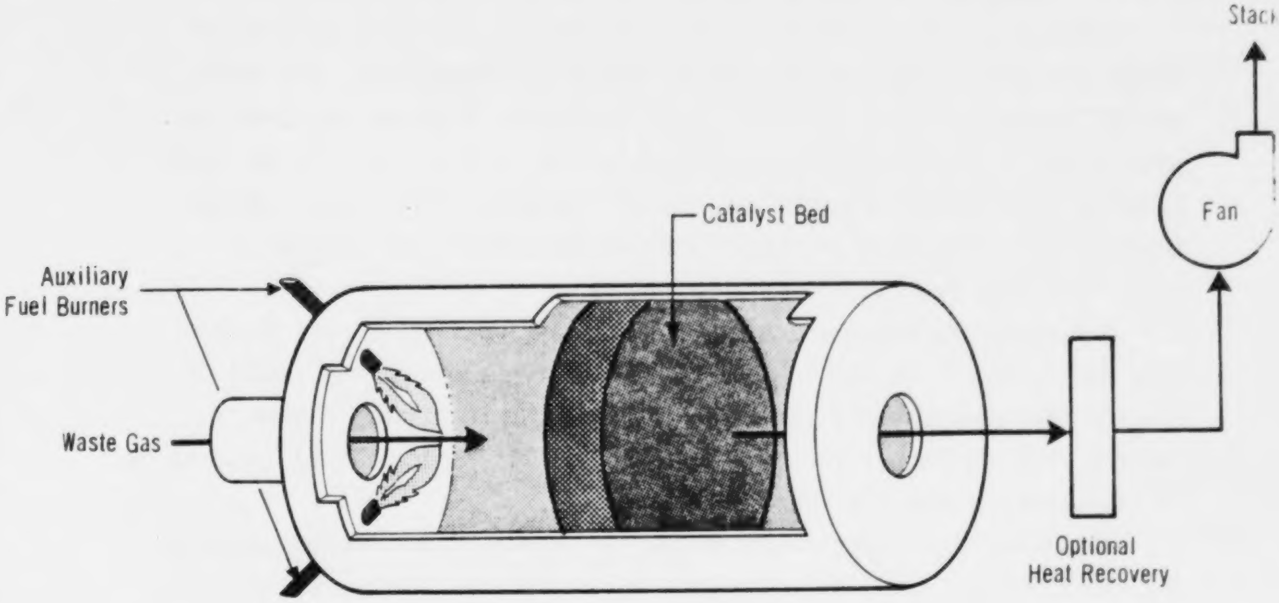
Stac
Fan
Catalyst Bed
Auxiliary
Fuel Burners
Waste Gas
Optional
Heat Recovery

Figure 4-7. Catalytic oxidizer.

4.5.4.2 Catalytic Oxidizer Emission Reduction Effectiveness

Catalytic oxidizers operating at 450°C (840°F) are able to oxidize waste gases as effectively as thermal oxidizers operating at 750°C (1380°F).[46] Catalytic oxidizer VOC destruction efficiencies of 95 percent have been reported in various cases and efficiencies of 97.9 to 98.5 percent are attainable in some systems.[47]

4.5.4.3 Parameters Affecting VOC Destruction Efficiency

Catalytic oxidizer destruction efficiency is dependent on catalyst volume per unit volume gas processed, operating temperature, and waste gas VOC composition and concentration. A typical catalyst bed contains about 0.014 to 0.057 m^3 of catalyst bed volume (0.5 to 2.0 ft^3) for each 28 Nm^3 m (1000 scfm) of waste gas flow.[48] Greater efficiencies can be attained by an increase in the volume ratio; however, the cost of a larger catalyst bed can become prohibitive.

The operating temperature range of combustion catalysts is usually from 316°C (600°F) to 650°C (1200°F). Lower temperatures may result in slowing down and possibly stopping the oxidation reaction. Higher temperatures may result in shortened catalyst life and possibly evaporation of the catalyst from the support substrate.

Accumulation of particulate matter or condensed polymerized material can block the active sites and reduce effectiveness. Catalysts can also be deactivated by compounds containing sulphur, bismuth, phosphorous, arsenic, antimony, mercury, lead, zinc, or tin.[49]

Conditions such as those noted above can result in VOC passing through or incomplete oxidation with the formation of aldehydes, ketones, and organic acids.

Sensitivity to waste stream flow condition variations and inability to handle moderate heating value streams limit the application of catalytic oxidizers as SOCMI air oxidation process vent emission controls.

4.5.5 Advantages and Disadvantages of Control by Combustion[51]

VOC control by combustion has several advantages: (1) a properly designed and operated combustion device can provide destruction of nearly all VOC; (2) most combustion units are capable of adapting to moderate changes in effluent flowrate and concentrations; and (3) control efficiency is insensitive to the specific VOC pollutant relative to product recovery techniques.

There are also disadvantages associated with VOC control by combustion: (1) high capital and operating costs result from thermal oxidation techniques, which could require a plot of land as large as 300 ft by 300 ft for installation; (2) since offgas must be collected and ducted to the afterburner, long duct runs may lead to condensation of combustibles and possibly to duct fires; and (3) since thermal oxidizers utilize combustion with a flame for achieving VOC destruction, the unit must be located at a safe distance from process equipment in which flammable chemicals are used. Alternatively, special designs may be employed to minimize the risk of explosion or fire.

There are several disadvantages particularly associated with control of halogenated VOC by combustion: (1) halogen acids produced by the combustion must be removed by flue gas scrubbing; (2) water and caustic are required at the site for scrubbing the flue gas; and (3) proper waste disposal of the salt formed during flue gas scrubbing is required.

4.6 TECHNICAL FEASIBILITY OF RETROFITTING CONTROL DEVICES[52-57]

In case of modified or reconstructed facilities, retrofitting of control equipment might be required by the NSPS. The difficulties encountered in retrofitting control devices are similar. Retrofit construction can involve demolition, crowded construction working conditions, scheduling construction activities with production activities, and longer interconnecting piping. Utility distribution systems and load capacities may not be adequate to accommodate the control equipment, and extra circuit breakers may be required.

Retrofitted control devices are preferably located on the ground near the process vents, but can be raised on platforms or mounted on the roof in order to accommodate other processes. There must be sufficient room around the units to allow for maintenance, and the exhausts must not present a hazard to equipment or personnel. Each requires electricity to operate fans, control and recording equipment. Valves and dampers may be pneumatically operated, requiring compressed air lines. Adsorption devices need steam for regeneration. Condensers probably need a refrigeration plant and coolant lines.

Retrofits may require remodeling of existing structures and coordination of the construction efforts with process operations.

Since thermal oxidizer systems require a relatively large land area and the safety aspects of an open flame are an important factor, the longer interconnecting piping probably is the most significant retrofit cost factor. Because offgas containing halogenated VOC requires combustion temperatures above those for which recuperative heat recovery is feasible, a waste heat boiler must be used for heat recovery. However, it may not be practical for all companies to utilize the heat recovery option. In a retrofit situation, it may be difficult to locate the waste heat boiler close to the steam-consuming site.

Data on retrofit requirements and costs for thermal oxidizers, recuperative heat exchangers, and waste heat boilers are given in Reference 57.

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30. Erikson, op. cit., p. IV-1.

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53. Erikson, op. cit., p. V-1.

54. Key, op. cit., p. III-1.

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5. MODIFICATION AND RECONSTRUCTION OF EXISTING FACILITIES

The proposed New Source Performance Standards (NSPS) will apply to all affected facilities, construction or modification of which commenced after the date of proposal of the NSPS. Provisions applying to modification and reconstruction were originally published in the Federal Register (FR) on December 23, 1971, clarifying amendments were proposed on October 15, 1974 (39 FR 36946), and final regulations were promulgated on December 16, 1975 (40 FR 58416).

A modification is defined as "any physical change in, or change in the method of operation of, an existing facility which increases the amount of any air pollutant (to which a standard applies) emitted into the atmosphere by that facility, or which results in the emission of any air pollutant (to which a standard applies) into the atmosphere not previously emitted."[1] Reconstruction occurs when components of an existing facility are replaced to such an extent that:

1. The fixed capital cost of the new components exceeds 50 percent of the fixed capital cost that would be required to construct a comparable entirely new facility.

2. It is technologically and economically feasible to meet the applicable standards.[2]

The purpose of this provision is to apply the standards to facilities that undergo such extensive reconstruction that they are essentially new sources. Failure to apply NSPS to these facilities would permit owners to construct such essentially new sources without installing best demonstrated technology.[3]

"In determining whether either a modification or reconstruction has occurred, the Agency focuses on the changes made to the piece or pieces of equipment that the NSPS defines as the "affected facility." If EPA determines that the "affected facility" has been modified or reconstructed, that facility alone -- rather than the whole plant -- must operate in compliance with the standards."

Under the following circumstances, an increase in emissions does not result in a modification:

1. If a capital expenditure that is less than the most recent annual asset guideline repair allowance (5.5 percent for chemical facilities) published by the Internal Revenue Service (Publication 534) is made to increase the production rate of an existing facility, even if an increase in emissions results, a modification is not considered to have occurred.

2. If an increase in hours of operation has occurred.

3. If the type of fuel or raw material has been changed, if this change does not involve a change in the original design of the facility. A facility shall be considered to be designed to accommodate an alternative fuel or raw material if that use could be accomplished under the facility's construction specifications as amended prior to the change. Conversion to coal required for energy considerations shall not be considered a modification.

4. If the increase in emissions results from maintenance, repair, or replacement which the Administrator determines to be routine for the source category.

5. If the facility relocates or changes ownership.

6. If the facility adds or uses any system or device whose primary function is the reduction of air pollutants (except when an emission control system is removed or is replaced by a system which the Administrator determines to be less environmentally beneficial).[4]

The air oxidation affected facility is defined as an individual process/product recovery train. Such a process/product recovery train would consist of an individual series or train of air oxidation product recovery equipment along with all air oxidation reactors feeding offgas into this equipment train. Each air oxidation reactor not feeding offgas into a product recovery train would constitute a separate affected facility. Each plant vent emitting any nitrogen which was introduced as air to the air oxidation reactor(s) would be included in an affected facility.

This chapter identifies and discusses some possible and/or typical changes to air oxidation processes of the Synthetic Organic Chemical Manufacturing Industry (SOCMI) which could be determined as being modifications or reconstructions. The magnitude of the industry covered and the complexity of the manufacturing processes permit only a general qualitative analysis. In addition, the list of modifications identified is by no means exclusive.

5.1 TYPES OF MODIFICATION

The 36 chemicals currently identified as being produced by air oxidation in the SOCMI have been screened to determine which of them are currently being produced by more than one commercial synthesis. Table 5-1, which lists these chemicals, was used to identify the following potential modifications:

1. Feedstock substitution.
2. Reactant substitution.
3. Catalyst substitution.
4. Process equipment changes.
5. Combinations of the above.

Table 5-1 also indicates the percentage of product produced by each process.

In the following sections, each type of modification is discussed and the probability of occurrence is delineated.

It is beyond the scope of this study to consider entirely new technology because of the difficulties in predicting their use.

5.1.1 Feedstock Substitution

A feedstock substitution is dictated by economics and the level of availability of the feedstock. Depending upon the specific process, a change in feedstock may require substantial capital investment to modify the process to accommodate the change. Table 5-1 shows that 10 chemicals have the potential for feedstock substitution.

5.1.2 Reactant Substitution

In several cases, the potential exists to substitute air for pure oxygen or chemical oxidants in the manufacture of SOCMI chemicals, or vice versa. Table 5-2 lists these chemicals and also indicates the percentage of product manufactured by each process.

Producing chemicals by air oxidation may have one or both of the following advantages over chemical and oxygen oxidation:

1. Air as a reactant is readily available at little or no cost.
2. Less costly construction material for the reactor to resist corrosion is required as compared to chemical oxidants.

TABLE 5-1. POSSIBLE FEEDSTOCK, REACTANT, AND CATALYST SUBSTITUTIONS IN AIR OXIDATION PROCESSES

Product	Feedstock	Reactant	Catalyst	Percentage of Production (%)
Acetaldehyde	ethylene	air	palladium chloride & cupric chloride	88
	ethanol	air	silver	8
Acetic Acid	acetaldehyde	air or oxygen	manganese or cobalt acetate	33
	butane	air or oxygen	manganese or cobalt acetate	46
Acetone	cumene	air	sulfuric acid	69
	isopropanol	air	metallic	29
1,3 Butadiene	n-butene	air	mixture of tin, bismuth, & boron, with phosphoric acid	7
	n-butane	air	chromia-alumina	13
n-Butyric Acid	butyraldehyde	air or oxygen		67
	n-butane	air		33
Formaldehyde	methanol	air	metallic-silver	77
	methanol	air	metal-oxide	23
Hydrogen Cyanide	propylene	air & ammonia		50
	methane	air & ammonia		50
Maleic Anhydride	benzene	air	70% vanadium pentoxide on inert carrier	85
	n-butane	air	proprietary information	15
Phenol	cumene	air	sulfuric acid	93
	toluene	air	cobalt-salt	2
Phthalic Anhydride	ortho-xylene	air	cobalt acetate	70
	naphthalene	air	combination of metal & promoter	30

TABLE 5-2. POSSIBLE REACTANT SUBSTITUTIONS

Product	Percentage of Product Manufactured By: Air Oxidation	Oxygen Oxidation	Others
Acetaldehyde	96		4
Acetic Acid	79 by air or oxygen oxidation		19
Acetone	98		2/5
Acrylic Acid/Phenol	90/95		10
1,3 Butadiene	20		80
n-Butyric Acid	33		
	67 by air or oxygen oxidation		
Cyclohexanol/ Cyclohexanone	75		25
Dimethyl Terephthalate	60		40
Ethylene Oxide	66	33	
Formic Acid/Methyl Ethyl Ketone	98/25		2/75
Glyoxal	Is produced by air, oxygen, and chemical oxidation		
Propionic Acid	8		92

In some instances, the reaction rate can be controlled better and thus, a better selectivity may be achieved by air oxidation. In other cases, energy requirements may be lower due to the fact that no separation of oxygen from nitrogen is required.

However, the major disadvantage of changing from oxygen or chemical oxidation to air oxidation is a substantial reduction of plant capacity. The substitution of air for oxygen results in a reduction of partial pressure in the reactor and, thus, in a lower driving force. In addition, air is not as strong an oxidizing agent as most chemical agents, resulting in a lower throughput, slower reaction, or different product mix. For air oxidation in the vapor phase, the plant capacity theoretically will be reduced by at least a factor of 4.76, unless the reactor pressure is increased. Furthermore, air oxidation would require larger equipment sizes to handle the inert nitrogen. These large equipment sizes would result in an additional cost for use of air oxidation, compared to oxygen oxidation.

Most chemical oxidation reactions are carried out in the liquid phase. When air is substituted for the chemical agent, this substitution may result in a phase change. In some instances, the catalyst will have to be changed when oxygen or chemical oxidation processes are converted into air oxidation processes. The selectivity also may change, resulting in a different product mix.

5.1.3 Catalyst Substitution

Research in SOCMI is mainly directed towards new catalyst development, although information on the state of the art in this field is not readily available. Catalyst changes can be made to improve product mix, reduce operating costs, or increase conversion rates.

A change in catalysts may cause significant variations in the quality and quantity of VOC emissions. Such a change may be accomplished in the existing reactor and may require major modifications in the reactor system and auxiliary process equipment.

Table 5-1 identifies six chemicals that show the potential for catalyst substitutions.

5.1.4 Process Equipment Changes

In the SOCMI air oxidation processes, changes in the process equipment may constitute a modification. Examples of such modifications are the replacement of a fixed-bed reactor with a fluidized-bed reactor, increasing the size of the reactor, and a change in the product recovery system from an absorber to a condenser or vice versa. These changes can result in increased VOC emissions, thus constituting a potential modification.

5.1.5 Combination of Modifications

In the majority of cases, a combination of the modifications described above will be chosen with the decision based on the most advantageous economics. The most common combination, to date, is a simultaneous change of feedstock and catalyst, although other combinations are possible and currently are encountered.

5.2 IDENTIFIED CHEMICALS

This section discusses on a chemical-by-chemical basis the extent to which the processes identified in Table 5-1 may be modified.

5.2.1 Acetaldehyde

Currently, 88 percent of acetaldehyde is produced by direct liquid phase oxidation of ethylene using a palladium chloride-cupric catalyst. In this process, the catalyst is regenerated with air or oxygen. Prior to the development of this process, acetaldehyde was produced by catalytic oxidation of ethanol in the vapor phase, which is an air oxidation. No new ethanol-based plants have been built since the ethylene-based process was developed[6] and, thus, no conversion of an ethylene-based plant to an ethanol-based plant will occur.

The conversion of an ethanol-based plant to an ethylene-based plant seems highly unlikely because such a conversion would be high in cost, involving a change in feedstock and catalyst as well as a phase change.

5.2.2 Acetic Acid

Currently, 19 percent of acetic acid is produced by a continuous liquid phase catalytic reaction of methanol and carbon monoxide, while 46 percent is produced by liquid phase catalytic oxidation of n-butane with either air or oxygen used as the oxidant and 33 percent is made by catalytic liquid phase oxidation of acetaldehyde with either air or oxygen used as the oxidant.[7]

As emphasized in the general discussion on reactant substitution, it appears highly unlikely that oxygen will be substituted by air as the oxidant, because this change would significantly reduce the plant capacity. A change in feedstock also seems unlikely because the n-butane-based process requires an absorber while the acetaldehyde-based process requires a
distillation column.

5.2.3 Acetone

Two major processes compete in the production of acetone: 1) oxidation/dehydrogenation of isopropanol and 2) co-production with phenol from cumene. Isopropanol accounts for approximately two-thirds of production, but co-production from cumene tends to control the price.[9] However, a conversion of an isopropanol-based plant to a cumene feed is highly unlikely because the production routes involve two entirely different processes. The isopropanol-based plant produces acetone by straight oxidation, while acetone is produced as a co-product from cumene via an intermediate hydroperoxide. In addition, a phase change and a change in pressure and temperature conditions is involved.

5.2.4 Acetophenone

To date, 60 percent of acetophenone is produced via air oxidation of ethylbenzene and 40 percent is made as a by-product in the cumene oxidation.[10] A change in production methods cannot be expected because the acetophenone is made as a by-product in the latter process and major modifications would be involved, in addition to entirely changing the product mix.

5.2.5 Acrylic Acid

Currently, 90 percent of the acrylic acid is made via air oxidation from propylene. Approximately 10 percent is produced by either the high- or low-pressure modified Reppe process, which is not an air oxidation process. Both modified Reppe processes are expected to be phased out[11] and replaced by new propylene-based air oxidation facilities.

5.2.6 Benzaldehyde

Benzaldehyde can be produced via air oxidation of toluene or via hydrolysis of benzyl-chloride.[12] Due to the entirely different processes, a conversion of a benzyl-chloride-based plant to a toluene-based plant will not occur.

5.2.7 1,3 Butadiene

1,3 Butadiene is predominantly formed as a by-product from olefins manufacture (80 percent), with the remaining 20 percent produced by air oxidation of n-butane (seven percent) and catalytic dehydrogenation of n-butane (Houdry process, 13 percent). The Houdry process does not constitute an air oxidation route, although air is utilized to regenerate the catalyst.[13]

It cannot be expected that the ethylene manufacturing process, of which 1,3 butadiene is a by-product, will be converted to a solely 1,3 butadiene manufacturing process. The conversion of the Houdry process to an air oxidation process does not appear feasible due to complex changes necessary in process equipment. This switch would involve a catalyst and feedstock change as well as the addition of a hydrocarbon adsorption column.

5.2.8 n-Butyric Acid

To date, 67 percent of n-butyric acid is produced by air or oxygen oxidation of butyraldehyde and 33 percent is produced by air oxidation of n-butane.[14] A conversion of an oxygen oxidation process into an air oxidation process is not feasible for reasons stated under the general discussion of reactant substitution. In addition, the n-butane process requires large separation equipment.

A change in feedstock does not appear likely because of different operating parameters. The oxidation of n-butyraldehyde is a low-temperature operation while high temperatures are involved in the oxidation of n-butane. In addition, different catalysts are used in both processes.

5.2.9 Cyclohexanol/Cyclohexanone

Currently, 75 percent of cyclohexanol/cyclohexanone is produced by air oxidation of cyclohexane with the remainder produced by hydrogenation of phenol.[15] Due to entirely different processes, a conversion of a phenol-based facility into an air oxidation facility is infeasible and, thus, not expected.

5.2.10 Dimethyl Terephthalate

Dimethyl terephthalate (DMT) is produced by air oxidation of para-xylene and methanol followed by crystallization and separation (60 percent) or by crude terephthalic acid (C-TPA) esterification with methanol, followed by fractional distillation (40 percent).[16]

Due to entirely different systems, no conversion of a C-TPA-based plant into a para-xylene-based plant is expected. The latter process would require the addition of a series of crystallizers and a high-pressure absorber.[16]

5.2.11 Ethylene Oxide

The production of ethylene oxide is an example of the possibility of a simple reactant substitution. To date, 66 percent is produced by air oxidation of ethylene while 34 percent is produced by oxygen oxidation of ethylene. Both processes are carried out in the vapor phase.[17]

The reasons why substituting air for pure oxygen is unlikely have been stated under the general discussion of reactant substitution.

Volumetric flow rates and vent gas compositions are compared in Table 5-3.

5.2.12 Formaldehyde

Formaldehyde is produced by air oxidation of methanol using a silver-metal catalyst (77 percent) or by air oxidation of methanol using a mixed-metal oxide catalyst (23 percent). The silver-metal process involves a combination of dehydrogenation and oxidation of methanol. The metal-oxide process involves oxidation of methanol. The major difference between the two processes is the amount of air mixed with the methanol before conversion. The metallic-silver catalyst process operates above the upper explosive limit, whereas the metal-oxide catalyst process operates below the lower explosive limit.[18]

The formaldehyde yield from the metal-oxide process is higher than that from the metallic-silver process and the process is simpler because methanol distillation is not required. However, the equipment costs for the metal-oxide process are greater because of the larger volume of gas stream.[19]

Volumetric flow rates of both processes and absorber vent gas compositions are compared in Table 5-4. If a metallic-silver catalyst is substituted by a mixed metal-oxide catalyst, VOC emissions will decrease and, thus, such a substitution would not constitute a problem. If a metal-oxide-based plant is converted to a metallic-silver-based plant, VOC emissions will increase and control equipment will be required.

TABLE 5-3. VENT GAS COMPOSITION FROM REPRESENTATIVE ETHYLENE OXIDE PLANTS*

Component	Air Oxidation Flowrate (kg/hr)	Air Oxidation Volume (%)	Oxygen Oxidation Flowrate (kg/hr)	Oxygen Oxidation Volume (%)
Nitrogen	59,619.0	87.7	54.8	16.2
Oxygen	2,278.5	2.9	20.0	7.3
Methane	--	--	2.3	1.5
Ethane	68.0	0.1	36.7	14.1
Ethylene	1,104.8	1.6	32.7	13.5
Ethylene Oxide	7.7	0.01	0.02	0.005
Carbon Dioxide	8,971.4	8.7	171.9	47.4
Total	72,049.4	100.0	318.4	100.0
Volumetric	917.6 m^3/min		3.2 m^3/min	

*Based on a production capacity of 90.7 x 10^6 kg/yr (1 x 10^5 tons/yr).

TABLE 5-4. ABSORBER VENT GAS COMPOSITION FROM REPRESENTATIVE FORMALDEHYDE PLANTS*

Component	Metallic-Silver Catalyst Flowrate (kg/hr)	Metallic-Silver Catalyst Volume (%)	Metal-Oxide Catalyst Flowrate (kg/hr)	Metal-Oxide Catalyst Volume (%)
VOC	24.41		16.29	
Formaldehyde	1.86	0.05	2.28	0.03
Methanol	4.60	0.11	9.98	0.14
Methyl Formate	11.74	0.14	--	--
Methylal	6.21	.10	--	--
Dimethyl Ether	--	--	4.09	0.04
Other Gases	3,000.40		5,875.81	
Oxygen	13.60	0.31	482.07	6.85
Nitrogen	2,814.98	74.35	5,244.93	85.02
Hydrogen	54.76	20.25	--	--
Carbon Monoxide	13.50	0.36	77.02	1.25
Methane	9.16	0.45	--	--
Water Vapor	94.40	3.88	260.53	6.57
Volumetric Flow	52.35 m^3/min		82.93 m^3/min	

*Based on a production capacity of 45 x 10^6 kg/yr.

This catalyst substitution, however, appears unlikely due to the different operating conditions. Such a catalyst substitution would involve a change in the air-to-methanol ratio, the operating temperatures, and either the addition of a distillation column or a larger absorber column.

5.2.13 Formic Acid

To date, 98 percent of the formic acid is produced as a by-product of acetic acid production by air oxidation of n-butane. The remaining two percent is produced by condensation reactions.[20] No conversion of a condensation facility to an air oxidation plant will occur due to entirely different operations.

5.2.14 Glyoxal

Glyoxal is currently manufactured by air or oxygen oxidation of ethylene glycol. A small percentage is made by chemical oxidation of acetaldehyde with nitric acid[21] which is a relatively new process. In general, conversion trends are toward new processes; therefore, no facilities are expected to convert from the new chemical oxidation process to the older air oxidation method.

5.2.15 Hydrogen Cyanide

Hydrogen cyanide is either produced by ammoxidation of methane (50 percent) or as a co-product by ammoxidation of propylene (50 percent).[22] Due to the fact that hydrogen cyanide is a co-product in one process and a single product in the other process, no conversion of facilities is expected.

5.2.16 Maleic Anhydride

The manufacture of maleic anhydride is an example of a feedstock substitution. Currently, 85 percent of maleic anhydride is produced by vapor phase air oxidation of benzene and 15 percent by butane oxidation.[23] It has been reported that the benzene feedstock can be replaced by n-butane in an existing facility by simply replacing the catalyst.[24] A distinct trend has been observed towards utilizing n-butane because this feedstock is readily available at a lower cost than benzene. Amoco Chemicals Corporation already produces maleic anhydride by the n-butane oxidation process. The process and the catalyst used in the plant are proprietary information; other facilities that have made this feedstock substitution are cited in the literature.[25-26]

Other reports mention significant differences between the two processes. The n-butane process is believed to require a longer reaction residence time and, thus, a bigger reactor.[27] Because of this, a higher capital investment may be required; however, no data are available to estimate the increase in cost.

Table 5-5 compares the offgas composition of the Amoco Chemicals Corporation plant with that of a typical plant using the benzene oxidation process. The offgas flow rates from both processes are approximately the same. The n-butane process does not emit any benzene; however, overall VOC emissions are about twice that of the benzene oxidation process. Thus, any change from benzene to n-butane would constitute a potential modification.

Due to the observed trend towards utilizing n-butane, the proposal of the NSPS could affect existing plants if they choose to convert from benzene to n-butane. However, a NESHAP for benzene has already been proposed requiring all existing facilities to control benzene emissions. Such facilities would probably use a thermal oxidizer to control benzene emissions. Thus, if a plant converts from the benzene process to the n-butane process after the NSPS has been proposed, it will already have a control device to control any additional VOC emissions. No upgrading of the control equipment will be required because the volumetric flow rate decreases (see Table 5-5).

5.2.17 Methyl Ethyl Ketone

To date, 25 percent of methyl ethyl ketone is manufactured as a by-product of air oxidation of butane while 75 percent is made by the dehydrogenation of secondary butanol.[28] Conversion of single-product processes to co-product processes is highly unlikely.

5.2.18 Phenol

Phenol is predominantly produced by air oxidation of cumene (93 percent). In addition, phenol is a by-product in the benzoic acid manufacture via air oxidation of toluene and in the manufacture of coal, tar, and petroleum.[29] No conversions are feasible.

TABLE 5-5. WASTE GAS COMPOSITION FROM REPRESENTATIVE MALEIC ANHYDRIDE PLANTS*

Component	Benzene		n-Butane	
	Flowrate (kg/hr)	Volume (%)	Flowrate (kg/hr)	Volume (%)
Organics	172.8	0.138	353.8	0.20
Benzene	133.0	0.083	--	--
Maleic Acid	5.6	0.002	--	--
Formaldehyde	28.7	0.047	--	--
Formic Acid	5.6	0.006	--	--
Other Gases	55,458.2	93.58	47,535.6	96.06
Oxygen	9,660.0	14.77	8,280.0	17.93
Nitrogen	42,518.0	74.29	36,444.0	77.00
Carbon Monoxide	1,350.3	2.36	1,654.2	0.47
Carbon Dioxide	1,292.9	2.16	1,654.2	0.69
Water Vapor	2,318.4	6.30	1,987.2	3.71
Total	57,949.4	100.00	49,876.6	100.00
Volumetric Flow	859.2 m^3/min		654.9 m^3/min	

*Based on a production capacity of 16.3 x 10^6 kg/yr.

5.2.19 Phthalic Anhydride

Currently, 70 percent of phthalic anhydride is produced via air oxidation of ortho-xylene in a fixed-bed reactor, while 30 percent of phthalic anhydride is produced via air oxidation of naphthalene in a fluidized-bed reactor. Both processes utilize a vanadium pentoxide catalyst. The ortho-xylene-based process operates below the lower explosive limit, and so uses a great excess of air, while the naphthalene-based process operates within the explosive limits by utilizing a fluidized-bed reactor.[30]

The ortho-xylene feed process is newer than the naphthalene feed process and will account for all or nearly all of the future growth in the industry. However, the older naphthalene feed process will continue to be operated by those producers who already have an investment in the process and a ready supply of naphthalene. Some plant conversions might occur, but it is not likely because the ortho-xylene process employs a fixed-bed tubular reaction system and the naphthalene process employs a coil-cooled, fluid-bed reaction system.[31]

Volumetric flow rates and switch condenser offgas compositions are compared in Table 5-6.

5.2.20 Styrene

To date, 10 percent of styrene is manufactured via air oxidation in co-production with propylene oxide. The remaining 90 percent is produced by catalytic dehydrogenation of ethylbenzene.[32] These two routes represent two completely different processes: the dehydrogenation process is a one-step operation while the air oxidation process involves several consecutive steps, each requiring separate reactors.

The conversion of a dehydrogenation process to air oxidation process is highly improbable because the changes in process equipment are too costly.

5.2.21 Terephthalic Acid

Terephthalic acid is predominantly produced by p-xylene air oxidation.[33] In newly developed process, which is not yet commercially available, terephthalic acid is produced by ammoxidation of p-xylene followed by a hydrolysis of terephthalamine.[34] No emission data from this process are available yet.

TABLE 5-6. SWITCH CONDENSER OFFGAS COMPOSITION FROM REPRESENTATIVE PHTHALIC ANHYDRIDE PLANTS*

Component	Xylene		Naphthalene	
	Flowrate (kg/hr)	Volume (%)	Flowrate (kg/hr)	Volume (%)
Phthalic Anhydride	167.3	0.0173	148.2	0.0321
Maleic Anhydride	315.4	0.0491	50.9	0.0167
Naphthalene	--	--	5.0	--
Benzoic Acid	20.4	0.003	--	--
Oxygen	32,819.1	15.69	12,208.2	12.24
Nitrogen	140,862.8	76.94	68,177.3	78.09
Carbon Monoxide	1,095.9	0.60	366.4	0.42
Carbon Dioxide	3,784.6	1.32	7,030.4	5.12
Sulfur Dioxide	34.1	0.01	--	--
Water	6,339.1	5.39	2,290.9	4.08
Total	185,438.7	100.00	90,277.3	100.00
Volumetric Flow	2,665 m^3/min		1,270 m^3/min	

*Based on a production capacity of 59 x 10^6 kg/yr.

5.3 SUMMARY

From the discussion above, it can be seen that all the changes described, with the exception of maleic anhydride, involve substantial changes in catalyst, reactor conditions, and product separation/purification equipment in addition to a switch in feedstock. The magnitude of these changes will probably make those kinds of potential modifications economically infeasible.

The substitution of n-butane for benzene in maleic anhydride manufacture appears to be driven by the rapidly rising price of benzene. The maleic anhydride NESHAP will require all benzene-based facilities to achieve a substantial reduction in benzene. The facilities would probably use a thermal oxidizer to achieve this emission control. If any benzene-based facilities switch to butane after the air oxidation standard is proposed, they will already have control and, thus, emissions should not increase.

Because raw material costs contribute significantly to the total product cost, much effort will be directed toward the search for cheaper, more readily available feedstocks (probably based on oil derivatives) in the next few years, due to the rapidly escalating price of gas and gas liquids. However, the chemical manufacturers will probably choose to build new facilities to utilize the cheaper feeds rather than go to the expense of radically modifying existing facilities.

No existing facilities are expected to undergo sufficient replacement of components to be considered a reconstructed facility. Any replacements would be expected to be limited to the reactor alone or to only one piece of product recovery equipment. The fixed capital cost of such replacement components would not be expected to exceed 50 percent of the fixed capital cost that would be required to construct a comparable entirely new facility.

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6. REGULATORY ALTERNATIVES

This chapter describes the method of regulatory analysis used for development of the air oxidation unit process NSPS and discusses the regulatory alternatives considered for controlling VOC emissions from SOCMI air oxidation process vent streams.

Many specific reaction types are used to manufacture the SOCMI air oxidation chemicals and, consequently, development of regulations for each chemical would be time-consuming and expensive. However, because air oxidation processes have many similar characteristics, especially the need to vent large quantities of inert material containing VOC to the atmosphere, an alternative approach, the unit process approach, is feasible. A unit process is a discrete, identifiable chemical reaction, such as nitration or oxidation, used in organic synthesis. The proposed air oxidation NSPS would regulate VOC emissions from all air oxidation unit processes (including the ammoxidation and oxychlorination processes). Air oxidation processes are those unit processes which either use air or a combination of air and oxygen as an oxygen source in combination with one or more organic reactants to produce one or more SOCMI chemicals. The air oxidation affected facility is defined as an individual process/product recovery train. Such a process/product recovery train would consist of an individual series or train of air oxidation product recovery equipment along with all air oxidation reactors feeding offgas into this equipment train. Each air oxidation reactor not feeding offgas into a product recovery train would constitute a separate affected facility. Each plant vent emitting any nitrogen which was introduced as air to the air oxidation reactor(s) would be included in an affected facility. Approximately 30 percent of all new or modified source SOCMI VOC emissions would be covered under the air oxidation unit process NSPS.[1,2]

6.1 METHOD OF REGULATORY ANALYSIS

According to the method of regulatory analysis developed for the air oxidation unit process NSPS, a national statistical profile, representing the air oxidation segment of SOCMI, was used to project the energy, economic, and environmental impacts associated with VOC control under several regulatory alternatives. Projection of these impacts was based on the use of a single VOC control technique, thermal oxidation. This section describes in detail the method of regulatory analysis used in the development of the air oxidation NSPS.

6.1.1 Unit Process Approach to NSPS Development

Typically, NSPS would be developed on a chemical-by-chemical basis. The manufacturing processes used by the single chemical-producing industry covered by such an NSPS would not differ greatly. It therefore would be possible to design a model plant that can be used to represent the emissions and control device requirements of typical new sources to be regulated. This model, along with a projection of the number of new sources coming on-line in a specified time period, would be used to analyze the economic, energy, and environmental impacts of control under several regulatory alternatives. These regulatory alternatives generally would be based on the use of several applicable control devices that can have different control efficiencies, costs, and energy requirements. The results of this analysis allow selection of the regulatory alternative that reflects the degree of emission limitation and the percentage reduction achievable through application of the best demonstrated technological system of continuous emission reduction, considering the costs, any nonair quality health and environmental impacts, and energy requirements. This regulatory alternative is then used as the basis for selecting a pollutant emissions limit and formulating the NSPS.

The unit process approach allows development of a standard that simultaneously regulates VOC emissions from all SOCMI air oxidation processes. Air oxidation facilities use 32 types of oxidation reactions to manufacture 36 different organic chemicals. Because of the number of facilities and processes to be covered, a chemical-by-chemical development of regulations for air oxidation production processes would require a considerable amount of time. Conversely, the unit process approach allows the resource-efficient development of a single, comparably effective standard that would cover a high percentage of SOCMI VOC emissions. In addition, this approach allows development of a standard that potentially would be applicable to SOCMI chemicals not currently produced by air oxidation processes.

6.1.2 Control Techniques

Industrial experience indicates that many types of control devices, including condensers, absorbers, adsorbers, and incinerators, can be used to reduce VOC emissions. Selection of the best VOC control device for a particular chemical manufacturing process and determination of the degree of control achievable depend on the chemical composition of the vent stream and other process characteristics. The vent stream flow rate and VOC concentration, the chemical and physical properties of the VOC and other contaminants, and the vent stream water content and temperature may greatly affect the specificity and effectiveness of devices such as condensers, absorbers, adsorbers, and catalytic incinerators. As a result, none of these potential control devices is suitable for reduction of VOC emissions from all air oxidation processes.

However, operation of a thermal oxidizer is much less dependent on these process and vent stream considerations and, consequently, is the only demonstrated VOC control technology universally applicable to SOCMI air oxidation processes. Furthermore, thermal oxidation can achieve the highest feasible VOC control level of all currently demonstrated technologies. Consequently, the regulatory analysis for this standard is based on the use of a single control device, a thermal oxidizer, to project the energy, economic, and environmental impacts of VOC control. Because thermal oxidizers are energy-intensive and relatively costly to operate, a regulatory analysis based on the use of this device will give conservative (higher) estimates of the costs and energy impacts associated with control of VOC emissions from air oxidation processes.

6.1.3 National Profile

One model plant would not have been sufficient for an accurate projection of the impacts associated with each regulatory alternative. Because of the number and diversity of facilities and manufacturing processes in the air oxidation industry, a large number of model plants would have been required. If the use of many model plants had been necessary, the prospective regulatory alternative analysis would have been predicted to take so much time that the unit process approach to regulation would have had little or no advantage over a chemical-by-chemical approach. However, only a limited amount of vent stream data is required to determine thermal oxidizer costs and efficiency. If it is assumed that the offgas contains no oxygen, the required data include offgas flowrate, net heating value, and VOC emission rate. It must also be known whether the offgas contains halogenated compounds. Therefore, although data from many types of processes are still required in order to adequately represent the air oxidation industry, the data need not consist of fully designed model plants. Rather, a national statistical profile of air oxidation processes was constructed. The national profile characterizes air oxidation processes according to national distributions of the three critical offgas parameters for halogenated and nonhalogenated vent streams. The impacts of each regulatory alternative are therefore evaluated as impacts upon the entire population of affected facilities, as represented by the national profile. The emission and production factors used to construct the data base for the statistical procedure and national profile are from existing air oxidation plants that represent about 36 percent of the total air oxidation plant population. Because there is no recognizable bias involving the four offgas parameters in this data sampling, this percentage of plants provides an adequate sample size to allow construction of a profile that is representative of the entire air oxidation part of SOCMI. Although the national profile is biased toward high volume products, correspondence with plants and EPA product reports indicate that the small-volume air oxidation chemicals do not differ significantly in the distribution of the four offgas parameters. Therefore, it is assumed that the overall distribution of key vent stream variables for the new air oxidation plants would be the same as that for the existing population.

The actual use of the national statistical profile assumes that the distribution of offgas flow, VOC emission rate, and stream heating value is chemical-independent. Chemical identities are not considered in the profile, nor is there claimed to be a one-to-one correspondence between any one data vector of three offgas parameters and an existing or new offgas stream. It is assumed, however, that the overall proportions and distributions of the parameter values and data vectors are similar to those of the new population of air oxidation facilities. Thus, since the national statistical profile contains 59 data vectors, each data vector represents 1/59 of the new population. Each data vector represents a hypothetical vent stream. Therefore, the impacts of a given regulatory alternative, such as annualized cost of control, VOC emission reduction, and facility cost-effectiveness, can be associated with each data vector. It is not assumed that such individual impacts on a data vector would represent impacts on any given new facility, nor are the data vectors used as individual impact models. Instead, the impacts of a regulatory alternative on a data vector represent 1/59 of the overall impact on the projected new population of facilities. Due to the wide variation in processes used and in the types of control devices present across the air oxidation industry, only uncontrolled emission factors and vent stream characteristics are included in the data set. Since uncontrolled emissions are subject to the greatest uncertainty because of the difficulty in defining what is a pollution control device, all stream data represent the process stream exiting the primary product recovery device.

The regulatory analysis for the air oxidation unit process NSPS based the projection of the impacts of emissions control on a cost- and energy-intensive control technique: thermal oxidation. Supplemental fuel costs and capital charges contribute the largest portion of the total annualized costs for VOC control using this technique. However, several other components add to the total resource burden that air oxidation plants would have to bear in controlling VOC emissions. These other components include electricity, labor, and (for offgas containing halogenated compounds) quench water, scrubbing water, and sodium hydroxide. Accordingly, this regulatory analysis focuses on total resource use in the selection of a regulatory alternative with acceptable energy impacts and total costs as well as acceptable emissions reduction. Air oxidation vent streams, therefore, were characterized further according to total resource-effectiveness (TRE), an index of the total resources required to destroy one unit of VOC by thermal oxidation.

The TRE index incorporates a measure of all resource requirements for VOC control. In addition to supplemental fuel and capital, this index takes into account electricity and labor, as well as quench water, scrubbing water, and sodium hydroxide for halogenated streams. The development of the TRE index is discussed in detail in Chapter 8, "Costs."

Vent streams with higher net heating values and VOC concentrations have lower supplemental energy requirements and higher achievable reductions in VOC emission rates than do more dilute streams. Therefore, TRE is lower for streams with higher net heating values and VOC concentrations.

For vent streams with similar net heating values and VOC concentrations, TRE decreases as flowrate increases. This relationship is due to the linear increase of achievable emission rate reduction with increasing flowrate, as well as economies of scale in thermal oxidizer capital costs as flowrate increases.

Use of the national profile to project the national energy, economic, and environmental impacts for all SOCMI air oxidation processes replaces the chemical-by-chemical determination of impacts for each chemical-producing industry covered by this unit process standard. Because the national profile is based on information available in a limited sample and data for some chemicals covered by the standard are not available, projection of national impacts was based on conservative assumptions to prevent understatement of the impacts associated with VOC control. Appendix F describes the statistical analyses and national profile in detail.

6.2 REGULATORY ALTERNATIVES

Regulatory analysis considers a variety of impacts associated with several alternatives for national VOC emissions control. These alternatives specify a range of control levels expressed as percentage reductions of national VOC emissions over the baseline level and are based on the use of a technically feasible control technique that is applicable to all affected air oxidation facilities. These levels of national VOC reduction are achieved by varying the percentage of facilities controlling VOC emissions using thermal oxidation at one level of control efficiency. Although the air oxidation NSPS will allow the use of equivalent technology to achieve the required VOC emission control, the regulatory analysis only projects energy, economic, and environmental impacts associated with the use of a thermal oxidizer. The operating conditions assumed included a temperature of 871°C (1600°F) with a chamber residence time of 0.75 seconds to achieve 98 percent VOC removal. For vent streams containing halogenated compounds, a combustion temperature of 1093°C (2000°F) with a residence time of one second was assumed. A VOC removal efficiency of 98 percent (or an incinerator outlet concentration of 20 ppmv) can be achieved by all new, properly designed incinerators operating at these conditions.[3-5]

A standard for control of VOC emissions from air oxidation process reactors and product recovery vents must reflect the degree of emission reduction achievable through application of the best system of continuous emission reduction considering the associated costs, nonair quality health and environmental impacts, and energy requirements. Regulatory analysis provides the background information necessary to determine this degree of emission reduction and to select the best alternative for VOC control with acceptable energy, economic, and environmental impacts. The alternative selected then provides the basis for recommending a VOC emissions limit and formulating the air oxidation NSPS. The following regulatory alternatives for control of VOC emissions from individual air oxidation facilities are considered:

1. Require no additional VOC control beyond the baseline level achieved under current state implementation plans (SIP). This alternative represents the level of control that would exist in the absence of any NSPS and is equivalent to about 72 percent national VOC reduction.
2. Require approximately 31, 46, 57, 66, 81, or 98 percent national VOC reduction from the baseline level based on the use of a thermal oxidizer at those air oxidation facilities required to meet a 98 percent VOC reduction requirement. These levels of national emissions reduction were chosen as convenient parameters for analysis.

Only a part of all air oxidation facilities would be required to control emissions to achieve the national VOC reduction over the baseline level specified under each regulatory alternative. The most stringent alternative requires 100 percent of all facilities affected by the air oxidation NSPS to control emissions and results in a 98 percent national VOC emission reduction from the baseline. The least stringent alternative requires 7 percent of all facilities to control emissions and causes a 31 percent national VOC emission reduction from the baseline. To determine which air oxidation facilities would be required to control VOC emissions to achieve the national emission reduction specified under each regulatory alternative, regulatory analysis uses levels of total resource-effectiveness (TRE). A resource-effectiveness cutoff level, which is an index of the maximum required total resource use per unit of VOC destroyed using thermal oxidation at affected individual air oxidation facilities, is computed for each regulatory alternative. Air oxidation facilities with total resource requirements which place them below the TRE index cutoff associated with a particular regulatory alternative would be required to control VOC emissions. Table 6-1 shows the percentage of facilities required to control VOC emissions and the TRE index cutoff associated with each level of national emission reduction. Because vent stream VOC content and heating value generally are related inversely to supplemental energy and capital requirements for VOC control, those streams containing the highest levels of VOC would be controlled before lower concentration streams, until the total amount of VOC removed gives the percentage reduction of national emissions required under a particular regulatory alternative. The TRE index, therefore, is used to achieve a national VOC emission reduction using the least possible amount of energy, capital, and other resources, by setting a limit on the amount of total resources to be used per unit VOC control by individual air oxidation facilities. From these considerations and by using the method of regulatory analysis described, the energy, economic, and environmental impacts of control were projected for each regulatory alternative.

The applicability to individual new facilities of an NSPS based on an acceptable regulatory alternative can be determined using the associated total resource-effectiveness index cutoff. Use of the TRE concept is meant to encourage the use of product recovery techniques or process modifications to reduce emissions. It will be possible for some air oxidation facilities to use product recovery techniques or process modifications to keep VOC emissions below levels that would require control as determined by total resource-effectiveness. Furthermore, certain facilities required to control VOC emissions are likely to use VOC control methods such as catalytic incineration or combustion in existing boilers and process heaters that are cheaper or less energy-intensive than thermal oxidation.

TABLE 6-1. REGULATORY ALTERNATIVES

Regulatory Alternative Baseline	Regulatory Alternative (Percent National VOC from Baseline)	Percent Facilities Required to Control VOC Emissions	Total Resource-Effectiveness Index Cutoff[a]
0	0	N/A	-
I	31	7	0.74
II	46	14	1.5
III	57	19	2.2
IV	66	27	3.1
V	81	47	6.2
VI	98	100	6,000

[a] The total resource-effectiveness (TRE) index is the cutoff value that defines facilities which must incinerate. The TRE index value defines the regulatory alternative that is referred to as the "percent national VOC reduction from baseline," because the TRE index value determines how the national emission reduction will be achieved. If the vent stream at an individual facility has a TRE index greater than the TRE index cutoff for a particular regulatory alternative, no VOC control would be required at that facility. However, if the TRE index is less than or equal to the TRE index cutoff, 98 percent VOC reduction or VOC reduction to 20 ppmv, whichever is less stringent, would be required.

6.3 REFERENCES FOR CHAPTER 6

1. Blackburn, J.W. Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry -- Air Oxidation Generic Standard Support. Hydroscience, Inc. EPA Contract No. 68-02-2577. May 1979. p. I-3, Table I-1.

2. Patrick, D.R. 2nd Year End Report -- Synthetic Organic Chemical Manufacturing Industry Standards Development Program. U.S. Environmental Protection Agency. Research Triangle Park, N.C., March 1979. p. 8.

3. Memorandum from Mascone, D.C., EPA:CPB. June 11, 1980. Concerning incinerator efficiency.

4. Blackburn, J.W. Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry -- Control Device Evaluation, Thermal Oxidation. EPA Contract No. 68-02-2577. July 1980.

5. Basdekis, H.S. Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry -- Control Device Evaluation, Thermal Oxidation Supplement. EPA Contract No. 68-02-2577. November 1980.

7. ENVIRONMENTAL IMPACT

This chapter discusses the environmental impacts of each regulatory alternative presented in Chapter 6. Impacts on air quality, water quality, solid waste, and energy requirements are analyzed. Regulatory analysis considers both the impacts attributed directly to a control device (e.g., reduced VOC emissions) and the indirect or induced impacts (e.g., aggravation of another pollutant problem through the use of a control device). The beneficial and adverse impacts of VOC control are examined, with emphasis on an accurate assessment of the national incremental impacts of the regulatory alternatives.

A comparison of the effects associated with each regulatory alternative on air and water quality, solid waste generation, and energy requirements provides a basis for selecting the highest degree of emission reduction achievable with acceptable environmental impact. The following range of increasingly stringent alternatives, including not setting a standard, was analyzed for controlling VOC emissions from air oxidation process vents:

1. Do not set a standard. This alternative assumes that VOC emissions from air oxidation process vents are controlled adequately to protect public health and welfare. This alternative represents the level of control achieved under State implementation plans (SIP's) and is equivalent to about 72 percent national VOC reduction. In estimating the baseline control level, it was assumed that current SIP's would remain in effect, except for areas requesting extension beyond 1982 for the ozone NAAQS. In these areas, it was assumed that SIP's would be modified to reflect the RACT recommendation of the air oxidation control techniques guideline (CTG) document. The baseline control fraction is derived in detail in Chapters 3 and Appendix F.

2. Require different percentages of all new air oxidation facilities to achieve 98 percent VOC control efficiency or 20 ppm (volume, by compound) outlet VOC concentration, whichever is less stringent. Based on increasing the percentages of facilities required to control VOC emissions, six regulatory alternatives, ranging from 31 to 98 percent national VOC emissions reduction from baseline, are defined.

A total resource-effectiveness (TRE) index associated with each regulatory alternative is used to determines which air oxidation facilities would be required to control VOC to achieve the specified national emissions reduction.

The environmental impacts associated with each level of national VOC emissions reduction were analyzed and presented. Because of the number and diversity of facilities and processes to be covered by this standard, no model plants were used. Rather, a national statistical profile representing the air oxidation segment of SOCMI, along with five-year industry growth projections, were used to estimate the 1986 environmental impacts for facilities built from 1982 to 1986. Appendix F describes the statistical analyses and national profile in detail.

Each regulatory alternative specifies a percent reduction of national VOC emissions from the baseline level that is achieved by requiring a percentage of new air oxidation facilities to reduce vent stream VOC emissions. The environmental impacts associated with each alternative were estimated assuming the use of a thermal oxidizer capable of achieving 98 percent VOC reduction at those facilities required to control VOC. The method of regulatory analysis is pesented in detail in Chapter 6, "Regulatory Alternatives."

7.1 AIR POLLUTION IMPACTS

This section presents both the beneficial and adverse effects on air pollution associated with the regulatory alternatives for control of VOC emissions from air oxidation process vents.

7.1.1 Effects of VOC Control on National Emissions

The primary environmental impacts of this standard would be beneficial and would consist of reduction in VOC emissions from SOCMI air oxidation processes. Regulatory analysis considered the projected mass emissions of VOC from air oxidation process vents. VOC emissions in 1986 from air oxidation facilities projected to be built during the preceding five years were estimated using the national statistical profile described in Appendix F.

The uncontrolled 1986 national VOC emissions from air oxidation process vents would be 78,000 Mg/yr (86,000 tons/yr). At the projected baseline control level, the national VOC emissions would be 22,000 Mg/yr (24,000 tons/yr). This baseline level of VOC emissions corresponds to a national VOC emission reduction of 72 percent from the uncontrolled level.

Table 7-1 shows the incremental VOC emissions for 1986 associated with each regulatory alternative. These alternatives are expressed as levels of national VOC emissions and national VOC emissions reductions from the baseline level. The percentage of air oxidation facilities that would be required to reduce vent stream VOC emissions to achieve the percent reduction of national VOC emissions from baseline specified under each regulatory alternative also are presented in Table 7-1.

The regulatory alternatives specify national emissions reductions that range from 31 to 98 percent VOC reduction from the baseline level. These control levels are achieved by requiring from 7 to 100 percent of all new air oxidation facilities to control VOC emissions. The least stringent regulatory alternative (31 percent national VOC reduction from baseline) would reduce national VOC emissions by 7,000 Mg/yr from baseline, resulting in national emissions of 15,000 Mg/yr. The most stringent regulatory alternative (97 percent give national VOC emission reduction from baseline) would require all new air oxidation facilities to control VOC emissions. This alternative would reduce national VOC emissions by 21,500 Mg/yr (48,000 tons/yr) from baseline, resulting national emissions of 440 Mg/yr.

7.1.2 Other Effects on Air Quality

Some adverse effects on air quality are associated with the use of a thermal oxidizer to reduce VOC. Pollutants generated by the combustion process, particularly nitrogen oxides (NO_x), may have an unfavorable impact on ambient air quality. The principal factors affecting the rate of NO_x formation are the amount of excess air available, the peak flame temperature, the length of time the combustion gases are at peak temperature, and the cooling rate of the combustion products.[1] The rate of NO_x formation is expected to be low due to the relatively low combustion temperatures and relatively short residence times associated with control of VOC using thermal oxidation.

TABLE 7-1. VOC EMISSIONS AND ENERGY REQUIREMENTS FOR SELECTED CONTROL LEVELS[a]

Regulatory Alternative (% National VOC Reduction from Baseline)	Percent of Facilities Required to Control VOC Emissions	National Emissions (10^3 Mg/yr)	National Emissions Reduction From Baseline (10^3 Mg/yr)	National Energy Impact (10^3 MJ/yr) (M BBL oil/day)	Energy-Effectiveness (10^3 MJ/Mg VOC Destroyed)	Maximum Energ Effectivenes (10^3 MJ/Mg VO Destroyed)
0	-	22	0	0 (0)	-	-
31	7	15	7	0.233 (0.110)	33	67.4
46	14	12	10	0.52 (0.24)	52	152
57	19	9.5	12.5	0.77 (0.36)	62	183
66	27	7.5	14.5	1.0 (0.46)	69	257
81	47	4.3	17.8	2.4 (1.10)	136	724
98	100	.44	21.5	6.0 (2.8)	278	463,468

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[a] Based on the use of a gas-fired thermal oxidizer operated 870°C (1600°F) with a chamber residence time of 0.75 seconds, or 1100°C (2000°F) and one second for vent streams containing halogenated compounds, to achieve a 98 percent VOC reduction at the individual facilities required to control emissions.

Thermal oxidizer outlet concentrations of NO_x were measured in seven sets of thermal oxidizer tests conducted at three air oxidation plants. The test results indicate that NO_x outlet concentrations range from 8 to 200 ppmv (0.015 to 0.37 g/m^3). These values could increase by several orders of magnitude in a poorly designed or operated unit. These tests are described and documented in Appendix C.

Although there are conflicting data, some studies report that incineration of vent streams containing high levels of nitrogeneous compounds also may cause increases in NO_x emissions.[2] The maximum outlet NO_x concentration of 200 ppmv was measured at an acrylonitrile plant. The vent stream of this plant contains nitrogeneous compounds. The NO_x concentrations measured at the other two plants, whose vent streams do not contain nitrogeneous compounds, range from 8 to 30 ppm (0.015 to 0.056 g/m^3).

Control of VOC emissions from oxychlorination process vent streams by thermal oxidation may result in the release of chlorinated combustion products to the environment. However, flue gas scrubbing can be used to remove these compounds from the incinerator outlet stream. Incineration temperatures greater than 871°C (1600°F) are required for destruction of halogenated VOC. At temperatures of 980° to 1100°C (1800° to 2000°F), almost all chlorine present exists in the form of hydrogen chloride (HCl). The HCl emissions generated by thermal oxidation at these temperatures can be removed efficiently by wet scrubbing.[3]

7.2 WATER POLLUTION IMPACTS

Control of VOC emissions using thermal oxidation does not result in any significant increase in wastewater discharge by air oxidation unit processes. No water effluents are generated by thermal oxidizers themselves.

Use of an incinerater/scrubber system for control of VOC emissions from oxychlorination process vent streams results in increased water consumption. In this type of control system, water is used to remove the HCl contained in the thermal oxidizer outlet stream. The increase in total plant wastewater would be relatively small and would not affect plant waste treatment or sewer capacity. However, if the absorbed HCl is not recoved, it may cause the water leaving the scrubber to have a low pH. This acidic effluent could lower the pH of the total plant effluent if it is released into the plant wastewater system.

The water effluent guidelines for individual States may require that industrial sources maintain the pH of water effluent within specified limits. To meet these guidelines, the water used as a scrubbing agent must be neutralized prior to discharge to the plant effluent system. The scrubber effluent can be neutralized by adding sodium hydroxide (NaOH) to the scrubbing water. The amount of NaOH needed depends on the amount of HCl in the waste gas. Approximately 1.09 kilograms (2.4 pounds) of NaOH are needed to neutralize 1 kilogram (2.2 pounds) of HCl. The salt formed must be purged from the system and properly disposed of. Most existing air oxidation facilities with halogenated vent streams currently incinerate and scrub the streams, and have State permits to dump the brine. It is projected that any new oxychlorination plants would be built in the same States that have given these brine-dumping permits. Acceptable methods of NaCl disposal include direct wastewater discharge or deep well disposal.[4] The increased water consumption and NaOH costs were included in the projected operating costs for those data vectors in the national profile representing halogenated vent streams. Costs associated with disposal of NaCl were not believed to be significant, and therefore, were not included in the projected impacts. The makeup rate for water purged from the system, based on 1 percent dissolved solids in the water recycle, is 0.033 m^3/kg (19.2 gal/lb) of chlorine in the waste gas.

The use of scrubbers to remove HCl from the incinerator offgas also could result in small increases in the quantities of organic compounds, such as ethylene dichloride, released into plant wastewater. Organic compound emissions into the water and, subsequently, into the air can be prevented by using a water stripper.

No increase in total plant wastewater is projected for those facilities which might use additional product recovery to achieve a total resource-effectiveness (TRE) value (discussed in Appendix E) above the 2.2 cutoff which corresponds to Regulatory Alternative III. Carbon adsorption is the only product recovery technique currently in use in the industry which has an associated organic wastewater effluent. Based on past industry experience, only three air oxidation chemical manufacturing processes are expected to employ carbon adsorption. Of these three processes only the maleic anhydride from benzene feedstock process might have a TRE value below the 2.2 cutoff associated with Alternative III. (Because of the other two processes, Alternatives IV, V, and VI might have a small associated water pollution impact.) However, if any new maleic anhydride facilities are built, it is projected they will utilize butane feedstock rather than benzene. The maleic anhydride from butane feedstock process would not use carbon adsorption for product recovery and therefore would have no additional wastewater.

If an existing benzene-feedstock maleic anhydride facility were modified or reconstructed (which is unlikely), such a facility might have a TRE value below the cutoff. In such an event, and if additional carbon adsorption were employed in lieu of incineration or some other type of product recovery, the adsorption unit of a typical maleic anhydride facility would generate approximately 500 Mg/yr of VOC which would be sent to wastewater treatment. The organic load of the wastewater from carbon adsorption would be less than 10 percent of the total liquid waste from such a facility. This wastewater stream could be treated along with the other plant effluent or recycled to the process. No new wastewater treatment plant or additional sewer capacity would be necessary.

7.3 SOLID WASTE DISPOSAL IMPACTS

There are no significant solid wastes generated or disposed of as a result of control by thermal oxidation. A small amount of solid waste disposal could result if catalytic oxidation were used by a facility, instead of thermal oxidation, to achieve an equivalent degree of VOC control. The solid waste would consist of spent catalyst. If a facility were to use an additional absorption column for improved product recovery in order to exceed a total resource-effectiveness (TRE) cutoff level, a small amount of solid waste would be generated by cleaning the column.

7.4 ENERGY IMPACTS

This section presents the national energy requirements associated with the regulatory alternatives for controlling VOC emissions from air oxidation process vents. Projection of the energy impact of each regulatory alternative is based on using a thermal oxidizer capable of 98 percent VOC reduction at those individual air oxidation facilities that would be required to control emissions. The 1986 energy requirements for controlling VOC emissions from air oxidation facilities expected to be built from 1982 to 1986 were estimated using the national statistical profile described in Appendix F.

7.4.1 Energy Requirements for Thermal Oxidation

Maintaining incinerator temperatures as high as 870°C (1600°F) for 0.75 seconds could be necessary to achieve the required 98 percent control efficiency. Supplemental fuel, commonly in the form of natural gas, is required to maintain the operating temperature. The amount of supplemental fuel needed depends on incineration temperature, type and amount of heat recovery, as well as offgas temperature, flowrate and heating value. Depending on the offgas characteristics, several types and levels of heat recovery assumed was 70 percent of the heat content of the incinerator outlet stream. Due to the use of steam-producing heat recovery techniques, combustion of some air oxidation vent streams results in a net production of energy even though supplemental fuel is necessary for flame stability. Facilities whose vent streams contain halogenated compounds generally employ such heat recovery for net energy produciton. However, energy-rich streams without halogenated compounds are not always net energy producers. Only that net production of energy resulting from control of vent streams containing halogenated compounds is included in the projection of national energy use. Supplemental fuel requirements account for most of the energy use.

Table 7-1 shows the incremental energy impacts for 1986 associated with each regulatory alternative. In addition to the total national energy requirement and the average energy-effectiveness, the table shows the highest energy-effectiveness for individual vent streams that would be subject to control under each alternative.

The energy-effectiveness for VOC control ranges from 33,000 MJ/mg of Voc destroyed for the 31 percent national VOC reduction alternative to 278,000 MJ/Mg of VOC destroyed for the 98 percent VOC reduction alternative. The corresponding annual national energy impacts range from .23 x 10^9 MJ/yr (110 bbl oil/day) to 6.0 x 10^9 MJ/yr (2,800 bbl oil/day) for the 31 percent and 98 percent VOC reduction alternatives, respectively.

Each maximum energy-effectiveness levels listed in Table 7-1 indicates the maximum projected supplemental energy, use by a facility, per megagram of VOC destroyed, for those facilities required to reduce VOC emissions under the given regulatory alternative. No individual air oxidation facility required to control VOC under a particular alternative would use a greater amount of supplemental energy than indicated by the corresponding maximum energy-effectiveness. Maximum energy-effectiveness increases gradually from 67,400 MJ/Mg of VOC destroyed for 31 percent national VOC reduction to 724,000 MJ/Mg of VOC destroyed for 81 percent VOC reduction. The remaining 7 percent national VOC reduction beyond 81 percent reduction is increasingly difficult to achieve in terms of energy requirements at individual air oxidation facilities. The maximum energy-effectiveness for 98 percent national VOC reduction would be 463,000,000 MJ/Mg of VOC destroyed. This alternative would require control at all air oxidation facilities.

7.4.2 Other Energy Requirements

Electricity requirements are approximately five percent of the total energy requirements included in the projected energy impacts. Electricity is required to operate the pumps, fans, blowers, and instrumentation that may be necessary to control VOC using a thermal oxidizer or a thermal oxidizer/scrubber system. Fans and blowers are necessary to transport vent streams and combustion air; pumps are necessary to circulate absorbent for incinerator/scrubber systems.

7.5 OTHER ENVIRONMENTAL IMPACTS

7.5.1 Considerations for Installing Control Equipment

Depending on the volume of offgas to be controlled, thermal oxidizers may require a site as large as 300 feet by 300 feet for installation. Because thermal oxidizers use combustion with a flame to control VOC emissions, these units must be located at a safe distance from process equipment using flammable chemicals, or special precautions must be taken to minimize the risk of explosion or fire.

7.6 OTHER ENVIRONMENTAL CONCERNS

7.6.1 Irreversible and Irretrievable Commitment of Resources

The use of thermal oxidation to control VOC emissions from air oxidation processes usually requires the use of supplemental energy in the form of natural gas or fuel oil. The adverse effects of using these non-renewable resources derived from petroleum must be considered when evaluating the benefits of controlling the release of potentially harmful air pollutants.

Use of the total resource-effectiveness concept to determine which air oxidation facilities would be required to control VOC is meant to encourage the use of product recovery techniques or process modifications to reduce emissions. Control of VOC emissions using product recovery techniques might be an alternative for some air oxidation facilities. Since the air oxidation vent streams containing VOC also are derived ultimately from petroleum, these techniques would result in conservation of both chemicals and fuels derived from petroleum.

7.6.2 Environmental Impact of Delayed Standards

If the air oxidation standard were delayed, significant adverse impacts on ambient air quality could result. Based on industry growth projections, air oxidation facilities controlling VOC emissions at current baseline levels (i.e., 72 percent national VOC reduction) would emit 22,000 Mg/yr (24,250 tons/yr) in 1986 compared to emissions of 440 Mg/yr for control under the most stringent regulatory alternative 98 percent national VOC reduction).

As stated in Sections 7.2 and 7.3, there are no significant water quality or solid waste impacts associated with the regulatory alternative. Therefore, there are no anticipated impacts in these areas resulting from delay of the standard.

Reducing VOC emissions from all air oxidation facilities by a 98 percent national reduction from the baseline level would require 6.0 x 10^9 MJ/yr (2,800 bbl oil/day). Although there is no accurate way to project the baseline energy impact, the energy use for VOC control if this standard were delayed would be significiantly less than that projected for control under the most stringent regulatory alternative.

7.7 REFERENCES FOR CHAPTER 7

1. Blackburn, J.W. Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry. Control Device Evaluation. Thermal Oxidation. EPA Contract #68-02-2577. July 1980. p. V-43.

2. Basdekis, H.S. Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry. Control Device Evaluation. Thermal Oxidation Supplement (VOC-Containing Halogens or Sulfur). EPA Contract #68-02-2577. November 1980. pp. II-4, II-6.

3. Basdekis, H.S., op cit., p. III-15.

4. Ibid.

8. COSTS

8.1 COST ANALYSIS OF REGULATORY ALTERNATIVES

8.1.1 Introduction

The cost impacts of implementing the seven regulatory alternatives for control of volatile organic compound (VOC) emissions from SOCMI air oxidation process vents are presented in this section. Capital costs, annualized costs, and cost-effectiveness of the regulatory alternatives are presented.

8.1.2 Substitution of National Profile for Model Plant

The cost impacts of the seven regulatory alternatives were estimated based on natural gas-fired thermal oxidation as the single control technique. For offgas that contains halogenated compounds, a design temperature of 1100^{0}C (2000^{0}F) and a residence time of 1.0 second were used. For offgas lacking halogenated compounds, a design temperature of 870^{0}C (1600^{0}F) and residence time of 0.75 second were used. A VOC destruction efficiency of 98 percent was used. The traditional model plant approach was not used. Because of the number and diversity of facilities and manufacturing processes in the air oxidation industry, a large number of model plants would have been required in order to accurately determine the cost impacts associated with the regulatory alternatives. However, only a limited amount of vent stream data is required to determine incinerator costs and efficiency. The required data include offgas flowrate, net heating value, and VOC emission rate. It must also be known whether the offgas contains halogenated compounds. Therefore, although data from many types of processes are still required in order to adequately represent the air oxidation industry, the data need not consist of fully designed model plants. Rather, a national statistical profile of air oxidation processes was constructed. The national profile characterizes air oxidation processes according to national distributions of the three critical offgas parameters for halogenated and nonhalogenated waste streams. The cost impacts of the regulatory alternatives are therefore evaluated as impacts upon the entire population of affected facilities, as represented by the national profile. The development and statistical basis for the national profile are described in detail in Appendix F.

8.1.3 Thermal Oxidation Design Categories[1-7]

The thermal oxidizer system design employed for a particular vent stream depends upon the offgas net heating value, the design flowrate, and the presence or absence of halogenated compounds. Sufficient fuel must be added to permit incineration at 870°C (1600°F). Fuel requirements can be reduced by the use of recuperative heat recovery to preheat the offgas and/or combustion air. Secondary heat recovery in addition to the heat exchanger is used by some facilities. However, use of secondary heat recovery was not assumed, in order to project conservative (higher) control costs. The basic design characteristics of each category are given in Table 8-1.

8.1.3.1 Categories A1 and A2

All vent streams which contain halogenated compounds are included in Categories A1 and A2. Due to the greater difficulty of achieving complete combustion of chlorinated VOC, an incineration temperature of 1100°C (2000°F) and a one second residence time were assumed. Combustion temperatures exceeding 870°C (1600°F) rule out the use of recuperative heat exchangers because of problems with materials of construction and with associated problems such as possible precombustion occurring in the exchangers. However, a waste heat boiler can be used effectively with temperatures to up to and above 1650°C (3000°F). The only air oxidation process which has chlorinated offgas is ethylene dichloride manufacture, which is known to employ waste heat boilers for heat recovery. Therefore, heat recovery in a waste heat boiler with steam generation was assumed. The amount of heat recovery was limited by a minimum outlet flue gas temperature of about 260°C (500°F), below which, excessive condensation of corrosive combustion products could occur.[8] The corrosive hydrogen chloride is then removed by flue gas quenching and scrubbing, and the resulting solution neutralized with caustic soda. Categories A1 and A2 do not differ in control system design, but only in supplementary fuel requirements.

8.1.3.2 Category B

Design Category B includes offgas with a heating value below 0.45 MJ/scm (12 Btu/scf), which corresponds to 25 percent of a typical lower explosive limit (LEL) in air.[9] For Category B, 70 percent heat

TABLE 8-1. BASIC CHARACTERISTICS OF EACH DESIGN CATEGORY[1-7]

Category	Minimum Net Heating Value (MJ/scm)	Maximum Net Heating Value (MJ/scm)	Incineration Temperature (°C)	Residence Time (Sec)	Type of Heat Recovery	Stream(s) Preheated	Percent Heat Recovery	Additional Control Equipment
A1[a]	0	3.3	1100	1.0	Waste-Heat Boiler	None	60%	Flue Gas Scrubber
A2[a]	3.3	-	1100	1.0	Waste-Heat Boiler	None	60%	Flue Gas Scrubber
B	0	0.45	870	0.75	Recuperative Heat Exchanger	Offgas and Combustion Air	70%	None
C	0.45	1.8	870	0.75	Recuperative Heat Exchanger	Combustion Air Only	34%	None
D	1.8	3.4	980	0.75	None	None	-	None
E	3.4	-	980	0.75	None	None	-	None

[a] Offgas contains halogenated compounds.

recovery was assumed. In this heating value range, the amount of heat recovery which could be used is only limited by a ceiling of about 550-600°C (1000-1100°F) on the combustion air preheat temperature due to burner design considerations.[10]

8.1.3.3 Category C

Because of insurance requirements, offgas with a heating value between 0.45 MJ/scm (12 Btu/scf) and 1.8 MJ/scm (49 Btu/scf), which constitutes Category C, may not be preheated.[11] This heating value range corresponds to a range of 25-100 percent of LEL in air for a typical organic vapor. Because air oxidation vent streams generally contain little or no oxygen, which is essentially depleted by the process reaction, offgas in this heating value range need not be diluted.[12] It was assumed that the combustion air would be preheated, with 34 percent of the flue gas heat content recovered.[13]

8.1.3.4 Category D

Offgas with a heating value in the range 1.8 MJ/scm (49 Btu/scf) to 3.4 MJ/scm (92 Btu/scf), which constitutes Category D, need not be preheated and requires only a small amount of auxiliary fuel, for flame stability. The offgas determines its own combustion temperature, which in general, exceeds 870°C (1600°F) and can be as high as 980°C (1800°F). A design temperature of 980°C (1800°F) was assumed, because of the larger chamber volume per mole of offgas and greater amount of refractory required at that temperature.

8.1.3.5 Category E

Design Category E includes offgas with a heating value above 3.4 MJ/scm (92 Btu/scf). Offgas in Category E need not be preheated and requires only a small amount of auxiliary fuel, for flame stability. The offgas, which determines its own combustion temperature, will burn at temperatures of 980°C (1800°F) or greater. Some processes and facilities with offgas this rich are able to use the steam which would be generated by employing a waste heat boiler after the thermal incinerator or by combusting in an existing boiler or process heater. Other facilities, however, will not be able to use steam and will not employ heat recovery. A few facilities might choose to dilute the offgas so that the flue gas temperature does not exceed 980°C (1800°F). In order to give a conservative estimate of costs, it was assumed that streams in Category E were diluted to 3.4 MJ/scm (92 Btu/scf), and that no heat recovery was employed.

8.1.3.6 Maximum Equipment Sizes

Because of shipping size restrictions, single thermal oxidizer units larger than about 32 feet by 16 feet would require field fabrication, which would greatly increase the cost.[14] Therefore, it is assumed that vent streams which would require larger incinerators would instead employ multiple sets of control equipment systems. The design standard temperature vent stream (incinerator inlet) flowrates, for each design category, which correspond to the maximum equipment size are given in Table 8-2.[15,16]

8.1.4 Offgas Composition Assumptions

Offgas with a flowrate less than 500 scfm are assumed to have a flowrate of 500 scfm for the purpose of calculating capital costs. In order to avoid underestimation of the required equipment sizes, all vent streams were assumed to contain no oxygen. Therefore, combustion air requirements were maximal. In order to increase the rate of combustion and avoid incomplete combustion and pyrolysis, it was assumed that enough excess combustion air was supplied to assure three mole percent oxygen in the flue gas.[17]

An average VOC molecular weight was calculated for the national profile.[18] Based on additional calculations by Enviroscience, all nonhalogenated VOC was assumed to consist of a typical model compound with the empirical formula $C_{2.8}H_{5.7}O_{0.63}$.[19] All halogenated VOC was assumed to consist of a typical compound with the empirical formula $C_{1.4}H_{2.4}Cl_{0.86}$.[20] Based on an inspection of the national profile, it was further assumed that each stream contained four moles of methane per mole of VOC. From these assumed offgas compositions, a typical ratio of flue gas flow to offgas flow was calculated for each design category and used to size the control equipment. These ratios are given in Table 8-3.[21,22] The model nonhalogenated VOC was assumed to have a net heating value of 71 MJ/scm, while a net heating value of 27 MJ/scm was assumed for the model halogenated VOC. These values correspond to net heating values of acetone and methyl chloride, respectively.[23,24] An offgas temperature of 38°C (100°F) was assumed.[25] These offgas composition assumptions were also used to determine the minimum and maximum net heating values for each design category. However, actual vent stream

TABLE 8-2. MAXIMUM OFFGAS FLOWRATES EACH DESIGN CATEGORY[15,16]

Category	Incineration Temperature (°C)	Residence Time (Sec)	Maximum Vent Stream (Incinerator Inlet) Flowrate (Thousand scm/min)
A1	1100	1.0	0.79
A2	1100	1.0	0.79
B	870	0.75	1.52
C	870	0.75	1.52
D	980	0.75	1.34
E	980	0.75	1.34

TABLE 8-3. RATIO OF FLUE GAS FLOWRATE TO OFFGAS FLOWRATE FOR EACH DESIGN CATEGORY[21,22]

Category	Maximum Net Heating Value (MJ/scm)	Incineration Temperature (°C)	Ratio of Flue Gas Flow to Offgas Flow[a]
A1[b]	3.3	1100	2.9
A2[b]	-	1100	2.9
B	0.45	870	1.9
C	1.8	870	2.3
D	3.4	980	2.5
E	-	980	2.5

[a] Both at standard temperature.

[b] Offgas contains halogenated compounds.

parameters were used in all other parts of the analysis. Actual offgas parameters were used in calculations for typical vent streams in each design category, regulatory alternative impacts, total resource-effectiveness projections, and process-specific economic analysis.

8.1.5 New Facilities

The installed cost impacts associated with each regulatory alternative are presented as impacts on the entire population of new facilities, as represented by the national profile.

8.1.5.1 Basis for Capital Costs

The capital costs for the implementation of the regulatory alternatives include purchase costs and installation costs for thermal incinerators, recuperative heat exchangers, ducts, fans, and stacks. For halogenated streams, the purchase and installation costs of waste heat boilers and flue gas scrubbers are also included.

The basic capital cost data was provided by the IT Enviroscience thermal oxidizer evaluation documents and was derived from vendor quotations.[26,27] The IT Enviroscience documents were specifically designed for air oxidation processes, which have vent streams containing little or no oxygen. Therefore, they take into account the maximum combustion air requirements for incineration of such streams. Furthermore, the Enviroscience documents present costs for a range of offgas heating values and incineration temperatures. Total installed costs are presented for two types and several levels of heat recovery. It was necessary to use a cost source possessing this flexibility to cover the variety of air oxidation vent stream characteristics. The Enviroscience costs were based on December 1979. In order to transform these to December 1978 dollars, an escalation factor of 0.900 was used. This factor is the ratio of the Chemical Engineering M&S chemical industry equipment cost index value for the fourth quarter, 1978, to that for the fourth quarter, 1979.[28]

The relation of the Enviroscience purchase cost estimates to the original vendor quotations is discussed in Appendix G. Graphs relating purchase costs to offgas flowrates are also given in Appendix G for each piece of control equipment. As discussed in that appendix, purchase cost estimates obtained from two additional vendors agreed well with the Enviroscience estimates.

Enviroscience estimates equipment installed costs from equipment purchase costs by adding factors for each of 10 aspects of installation. These factors are expressed as percentages of the equipment purchase cost. The most important factors are those for piping and erection. A list of the installation components for which factors were developed is given in Table 8-4.[29] A detailed discussion of the derivation and use of the installation factors is given in Appendix G.

The total installed capital costs represent the total investment, including all indirect costs such as engineering and contractors' fees and overheads, required for purchase and installation of all equipment and material to provide a facility as described. These are battery-limit costs and do not include the provisions for bringing utilities, services, or roads to the site, the backup facilities, the land, the research and development required, or the process piping and instrumentation interconnections that may be required within the process generating the waste gas feed to the thermal oxidizer.[30]

The basis for the capital costs is further discussed below for each design category. Total installed capital cost equations as a function of operating offgas flowrate are given in Table 8-5 for each design category. It was assumed that a typical operating offgas flowrate would be 95 percent of the design maximum. Therefore, a design vent size factor of 0.95 was assumed to avoid an underestimate of control equipment size and capital cost. These capital cost equations were obtained by fitting an analytical function of capital cost versus design offgas flowrate to the data in the Enviroscience tables and graphs. A different cost curve was fit for each design category.

All three coefficients were estimated for the Category B equation. The exponent was estimated to be 0.88. This exponent was assumed for the other design categories, and only the remaining two coefficients were fit for them. These equations are judged to be reasonably close fits, and no claim is made that they are the best ones that could have been statistically determined. Capital cost estimates for a hypothetical vent stream with characteristics which are average for each design category are presented in Table 8-6.

Several pieces of control equipment are common to each design category. These include the thermal oxidizer, ducts, fans, and stack.

TABLE 8-4. INSTALLATION COMPONENTS

Installation Component
Foundation
Insulation
Structures
Erection
Piping
Painting
Instruments
Electrical
Fire Protection
Engineering, Freight and Taxes

TABLE 8-5. TOTAL INSTALLED CAPITAL COST EQUATIONS AS A FUNCTION OF OFFGAS FLOWRATE[29,30]

Category	Maximum Flowrate Per Unit (Thousand) (scm/min)	Fabricated Equipment Cost Escalation Factor	Design Vent Size Factor	C1	C2	C3
A1	0.79	.900	.95	802 70	15.2[a]	0.88
A2	0.79	.900	.95	802.70	15.2[a]	0.88
B	1.52	.900	.95	259.89	3.94	0.88
C	1.52	.900	.95	288.78	2.49	0.88
D	1.34	.900	.95	242.27	3.11	0.88
E[b]	1.34	.900	.95	242.27	3.11	0.88

Total Installed Capital Cost (\$1000) = (# of Units) x (Escalation Factor) x

$$(C1 + C2 \times ((\text{Flowrate } (\tfrac{\text{scm}}{\text{min}}) \div \text{Design Vent Size Factor})^{C3}))^{c}$$

[a] Flowrate Correction Factor of 1.12 = $(1.14)^{.88}$ Incorporated into Coefficient C2.

[b] Dilution Flowrate is Used in Capital Cost Equation.
Dilution Flowrate = (Design Flowrate) x (Original Heating Value) ÷ (3.5 MJ/scm).

[c] Flowrate per equipment unit.

TABLE 8-6. INSTALLED CAPITAL COSTS FOR A SELECTED HYPOTHETICAL VENT STREAM IN EACH DESIGN CATEGORY[29,30]

Category	Offgas Heating Value (MJ/scm)	Vent Stream Flowrate (scm/min)	Number of Equipment Units	Dilution-Corrected Flowrate Through Each Equipment Unit (scm/min)	Overall System Installed Capital Cost ($1000)[a]
A1	0.69	456	1	456	3,900
A2	4.21	456	1	456	3,900
B	0.22	456	1	456	1,200
C	1.11	456	1	456	780
D	2.56	456	1	456	860
E	4.5	456	1	608	1,000
B, Two Equipment Units	0.22	1,609	2	805	2,600

[a] Including all auxiliary equipment.

The thermal oxidizer consists of a refractory-lined carbon steel mixing chamber and combustion chamber. Discrete burners are assumed. Enviroscience assumed a 10 percent heat loss from the combustion chamber for all combustion temperatures and design categories.[31]

The ducts consist of 150 ft of round-steel inlet with four ells, one expansion joint, and one damper with control.[32] Considerably more ductwork may be required in some cases. However, ductwork accounts for only two to eight percent of the total installed capital cost. Therefore, the total installed capital cost is relatively insensitive to the amount of ductwork.

Fans are included for both offgas and combustion air.[33] Costs for motors and starters are included. The offgas flowrate, combustion air flowrate (calculated from the flue gas to offgas flow ratio) and pressure drop of the thermal oxidizer are used to calculate fan sizes. For vent streams in Category A, which require flue gas scrubbing, the pressure drop across the scrubber is also considered.

The stack design height is 80 ft.[34] A superficial linear gas velocity of 15 m/sec (3000 ft/min) is assumed in calculation of the cross-sectional area.

Streams in Categories A1 and A2 require flue gas quenching and scrubbing to remove corrosive hydrogen chloride. A waste heat boiler is employed for heat recovery prior to quenching. An overall heat transfer coefficent of 0.16 $\mathrm{MJ/(hr{\cdot}m^2{\cdot}{}^\circ C)}$ (8 $\mathrm{Btu/(hr{\cdot}ft^2{\cdot}{}^\circ F)}$ is assumed for the boiler.[35] Steam is generated at 120°C (250°F) and a pressure of 1.7 $\mathrm{MN/m^2}$ (250 psi). For 60 percent heat recovery, the ratio of heat exchange surface area to flue gas flowrate is 0.89 $\mathrm{m^2/scm}$ (0.27 $\mathrm{ft^2/scfm}$). The scrubber column design is based on 36 ft of packing.[36] The liquid-to-gas ratio is assumed to be 10. A superficial vapor velocity of three ft/sec was used for determining the column diameter. The quench chamber design location is the lower part of the scrubber column.[37] It has the same diameter as the scrubber column. A one second flue gas retention was assumed. In reducing the flue gas temperature to the adiabatic saturation temperature of the scrubbing agent, considerable water is vaporized, increasing the gas flow through the scrubber. The ratio of quenched to unquenched flue gas (both standard) flowrate is 1.67 at 1100°C (2000°F).

Vent streams in Category B employ 70 percent recuperative heat recovery.[38] The heat exchanger tubes are constructed of carbon steel, except for the first few passes. It is necessary to construct the tube regions which experience a flue gas temperature between 820 and 870°C (1500 and 1600°F) of heat-resistant nickel alloy. An overall heat transfer coefficient of 0.08 $MJ/(hr \cdot m^2 \cdot {}^oC)$ (4 $Btu/(hr \cdot ft^2 \cdot {}^oF)$) is assumed for the heat exchanger. This assumption is deliberately low, and hence the heat exchanger is deliberately over-designed to some degree. For 70 percent heat recovery, the ratio of heat exchange surface area to flue gas flowrate is 2.7 m^2/scm (0.83 ft^2/scfm). Recuperative heat recovery reduces both the natural gas and combustion air requirements of the thermal oxidizer. Therefore, the required combustion chamber volume is reduced. For 70 percent heat recovery, the combustion chamber size reduction factor is 0.667 (corresponding to a 33 percent reduction in system size relative to no heat recovery).

Vent streams in Category C are assumed to preheat the combustion air only, due to insurance requirements for safe handling of offgas with VOC concentrations above 25 percent of LEL in air.[39] Thirty-four percent heat recovery is assumed. Materials of construction and overall heat transfer coefficient are the same as in Category B. For 34 percent heat recovery, the ratio of heat exchanger surface area to flue gas flowrate is 1.2 m^2/scm (0.36 ft^2/scfm). The combustion chamber size adjustment factor is 0.81 (corresponding to a 19 percent reduction in system size relative to no heat recovery).

Due to their high heating value, vent streams in Category D determine their own combustion temperature. A temperature as high as 980°C (1800°F) may be reached. Therefore, preheating of the offgas is not economically advantageous, nor is it technically feasible at temperatures above 870°C (1600°F). It was not assumed that any process with offgas in Category D could use generated steam, and therefore no waste heat boiler was included in the design. The combustion chamber design takes into account the extra refractory and internal volume required by the higher incineration temperature.

Vent streams in Category E are assumed to be sufficiently diluted prior to combustion that the resultant offgas heating value is 3.6 MJ/scm (98 Btu/scf), so that the flue gas temperature will not exceed 980°C (1880°F). The correction equations are:

1. New flowrate = (old flowrate) x (old heating value) ÷ (3.6 MJ/scm),
2. New % VOC = (old % VOC) x (old flowrate) ÷ (new flowrate), and
3. New heating value = 3.6 MJ/scm.

The same incinerator design is assumed as in Category D.

8.1.5.2 Basis for Annualized Costs[40,41]

The typical annualized costs consist of the direct expenses for operating labor, utilities, and maintenance materials and labor plus the indirect costs for overhead, taxes, insurances, general administration, and the capital recovery charges. The utilities include natural gas and electricity. For Category A, scrubbing water, quench makeup water, and caustic are also included. Return on investment for the control equipment is not included. All the data required in the estimation of these cost factors and costs were obtained from References 40 and 41. The annualized cost factors are given in Table 8-7. Those operating factors which vary with design category are given in Table 8-8. The equations used to calculate annualized costs are given in Table 8-9.

Costs associated with disposal of sodium chloride from the neutralized scrubbing water of halogenated vent streams (Categories A1 and A2) are not included in the annualized costs. These disposal costs would vary widely from facility to facility. However, sodium chloride disposal costs are insignificant in almost all existing plants.

IT Enviroscience developed natural gas use curves and tables from a detailed heat and material balance.[42,43] The Enviroscience work was checked for vent streams with heating values at the cutoff points distinguishing design Categories B, C, D, and E, as well as for chlorinated streams (Categories A1 and A2). For these cutoff cases, the heat and material balance was completely redone, using a slightly different set of assumptions.[44] These different assumptions included that of no preheating of the offgas for Category C streams. The common assumptions are presented above in Section 8.1.4. A further discussion of the heat and material balance calculation is given in Reference 45.

TABLE 8-7. ANNUALIZED COST FACTORS[40-41]

December 1978 Dollars

Direct

Operating Labor: \$13.08/hr (Includes Overhead)[a]

Operating Labor Factor: 2400 Labor-hr/yr (Categories A1-A2)
2133 Labor-hr/yr (Categories B-C)
1200 Labor-hr/yr (Categories D-E)

Electricity: \$0.02616/kWh[a]

Natural Gas: \$4.78/Thousand MJ[e]

Heat Recovery Credit: \$4.78/Thousand MJ

Quench Water Price: \$0.22/Thousand Gallons[a]

Scrubbing Water Price: \$0.22/Thousand Gallons[a]

Caustic Price: \$0.0436/lb[a]

Maintenance Labor Plus Materials Factor = .06 of Total Installed Capital

Indirect ("Capital Charges")

Interest Rate = i = 8.5% (After Taxes)[b]
= 10% (Before Taxes)[c]

Incinerator Lifetime = 10 Years = N

$$\text{Capital Recovery Factor} = \frac{i\,(1+i)^N}{(1+i)^N-1} = 0.152 \text{ (After Taxes)}^b$$

$$= 0.163 \text{ (Before Taxes)}^c$$

Taxes, Insurance and Administrative Charges Factor = .05 of Total Installed Capital

Overall Capital Charges Factor = .213 of Total Installed Capital

Overall Taxes and Maintenance Factor = .11 of Total Installed Capital

Possible Annual Operation = 8760 hr/yr

Average Capacity Utilization Factor for Air Oxidation Industry = .77[d]
(Multiplied by Possible Annual Operation to Give Actual Average Annual Operation)

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[a] Corrected from Enviroscience values (in December 1979 dollars) to December 1978 dollars by a deflation factor of 0.872.

[b] After tax interest rate and capital recovery factor used in process-specific economic analysis (Chapter 9) and calculating typical costs for facilities in each design category.

[c] Before tax interest rate and capital recovery factor used in calculating national cost impact for each regulatory alternative.

[d] Memo to Hurley, E., EEA, from Galloway, J., EEA, January 13, 1981.

[e] Galloway, J., EEA telecon with Robson, J., EPA:EAB, July 13, 1981. Discussion on natural gas prices.

TABLE 8-8. OPERATING FACTORS FOR EACH DESIGN CATEGORY[40,41]

Category	Minimum Net Heating Value (MJ/scm)	Maximum Net Heating Value (MJ/scm)	Ratio of Flue Gas Flow to Offgas Flow[a]	Minimum Heat Recovered (MJ/scm)	Pressure Drop (Inches H_2O)[42,43]	Labor Cost ($1,000/yr)	Natural Gas Use Coefficients G0	G1	G2	G3
A1[b]	0	3.3	2.9	3.38	22[c]	31.39	0	4.53	-0.985	0
A2[b]	3.3	-	2.9	3.38	22[c]	31.39	0	0.329	0	0
B	0	0.45	1.9	0	10[d]	27.90	0.425	0.666	-1.29	0.015
C	0.45	1.8	2.3	0	10[d]	27.90	0	2.39	-1.22	0
D	1.8	3.4	2.5	0	6[e]	15.70	0	0.183	0	0
E	3.4	-	2.5	0	6[e]	15.70	0	0.183	0	0

[a] Both at standard conditions.

[b] Offgas contains halogenated compounds.

[c] Includes 6 inches across the combustion chamber, 4 inches across the waste heat boiler, and 12 inches across the scrubber.

[d] Includes 6 inches across the combustion chamber and 4 inches across the recuperative heat exchanger.

[e] Across the combustion chamber.

TABLE 8-9. ANNUALIZED COST EQUATIONS[40,41]

Operating flowrate (Nm^3/min) = Design flowrate (Nm^3/min) x Capacity Utilization Factor

In the following Operating Cost and emissions equations, "flowrate" means the operating flowrate per equipment unit (dilution flowrate for Category E)

National Gas Used (TJ/yr) = $0.5256\ \frac{\text{Million Min}}{\text{yr}} \times \left(G0 + \text{Flowrate} \times \left(G1 + G2 \times \text{Heating Value} + G3 \times \text{Heating Value}^2\right)\right)$

Natural Gas Cost ($1,000/yr) = Natural Gas Price ($/GJ) x Natural Gas Used (TJ/yr)

Labor Cost ($1,000/yr) = Labor wage ($/man-hr) x Operating labor factor (man-hr/yr) ÷ 1,000

Electricity Cost ($1,000/yr) = 0.0604 x Electricity Price ($/kWh) x Pressure Drop (inches H_2O) x flowrate (Nm^3/min) x flue-gas/offgas ratio

Quench water cost ($1,000/yr) = Quench water price ($/thousand gal) x flowrate (Nm^3/min) x 0.00886 x flue-gas/offgas ratio

Scrubbing water cost ($1,000/yr) = Scrubbing water price ($/thousand gal) x flowrate (Nm^3/min) x 0.289 x flue-gas/offgas ratio

Caustic cost ($1,000/yr) = Caustic Price ($/lb) x flowrate ($Nm^3$/min) x 17.17 x flue-gas/offgas ratio

Heat recovery credit ($1,000/yr) = Natural Gas Price ($/GJ) x Heat Recovery Factor (MJ/Nm^3) x flowrate (Nm^3/min) x 0.5256 (Million min/yr)

Taxes and Maintenance Cost ($1,000/yr) = Installed Capital ($1,000) x Taxes and Maintenance Factor

Operating Cost ($1,000/yr) = Taxes and Maintenance Cost ($1,000/yr) + Number of equipment units x Gas Cost + Labor Cost + Electricty Cost + Quench Cost + Scrub Cost + Caustic Cost - Heat Recovery Credit

Annualized Cost ($1,000/yr) = Operating Cost + Capital Recovery Factor x Capital Cost ($1,000)

Hourly Emissions (kg/hr) = 0.0268 (moles/Nm^3) (min/hour) (kg/g) (1/100%) x Flow (Nm^3/min) x (% VOC) x (Molecular Weight)

Annual Emissions (Gg/yr) = Hourly Emissions (kg/hr) x 365 days/year x 24 hours/day x 1 Gg/10^6kg

Annual Emission reduction (Gg/yr) = Annual Emission (Gg/yr) x 0.98

Cost Effectiveness ($/Mg) = Annualized Cost ($1,000/yr) ÷ Annual Emission Reduction (Gg/yr)

The results of the recalculations for the critical cases were essentially in agreement with the Enviroscience work. Because of the necessity of calculating fuel requirements and costs for the entire national statistical profile of 59 vent streams (discussed in Appendix F), detailed heat and mass balances were not done for each stream. Instead, equations were fit to the Enviroscience tables and graphs of natural gas use. The coefficients of the fuel-use equation are given in Table 8-8.

Streams in Categories D and E have sufficient heating value that they only require a small amount of fuel, for flame stability. The fuel requirement for these streams was assumed to be equivalent to 0.18 MJ of natural gas heat per standard cubic meter of offgas, independent of offgas heating value. This fuel requirement was chosen because it is equivalent to that calculated according to the Category C fuel use equation for offgas with a heating value of 1.8 MJ/scm (which is the cutoff heating value distinguishing Categories C and D). Therefore, a composite graph of the fuel use equations for Categories C and D versus offgas heating value would not be discontinuous at the cutoff heating value.

For the chlorinated streams in Categories A1 and A2, Enviroscience did not develop heat and mass balance calculations for the designated combustion temperature of 1100°C, but only for higher temperatures. Therefore, the fuel requirements were interpolated from the curves for 980°C and 1200°C. A fuel use equation was fit to this interpolated curve. This equation indicates that chlorinated offgas with a heating value greater than 3.3 MJ/scm requires primarily auxiliary fuel, for flame stability. At this critical heating value, according to the fuel use equation, the amount of fuel required per normal cubic meter of offgas is equivalent to 10 percent of the offgas heating value, which is a typical auxiliary fuel requirement.[46] This heating value constitutes the cutoff between design Categories A1 and A2. For Category A1, the fuel use equation discussed above was employed. For Category A2, the fuel requirement was assumed to be equivalent to 0.33 MJ of natural gas heat per normal cubic meter of offgas, independent of offgas heating value.

The assumption of a maximum heat exchange efficiency of 70 percent may be conservative for some facilities. A thermal oxidation system employing regenerative heat recovery could achieve a primary heat exchange efficiency as high as 85 to 95 percent.[47] Therefore, facilities able to employ such technology would have substantially lower fuel requirements.

Several additional conservative assumptions are built into the fuel use equations. The most important is the assumption of no oxygen in the offgas. This leads to maximum combustion air requirements and a higher total incinerator inlet flow to be heated to the combustion temperature.

8.1.5.3 Emission Control Costs

This section discusses the estimated emission control costs associated with control by thermal oxidation of a typical vent stream for each design category. These emission control costs are given in Table 8-10. The control costs are broken down into detailed components, including all types of operating expenses, capital charges, and heat recovery credits.

The primary contributors to the annualized costs for the typical chlorinated, dilute Category A1 stream shown in Table 8-10 are capital charges and caustic costs. These account for about 36 percent and 25 percent, respectively, of the total annualized costs. For the chlorinated, concentrated Category A2 stream shown in Table 8-10, capital charges and caustic costs are the primary contributors to total annualized costs. The sum of the other contributors is negative due to the very large heat recovery credit. For the dilute Category B streams which employ 70 percent heat recovery to reduce fuel requirements, natural gas costs account for 55 percent of the total annualized cost. Capital charges account for about 30 percent of the total annualized cost. The moderately dilute streams of Category C, which cannot employ preheating of the offgas because of safety considerations, have higher energy requirements, relative to capital charges, than do Category B streams. For the typical stream shown in Table 8-10, gas costs account for about 76 percent of the total annualized cost, while capital charges account for about 14 percent. The VOC-rich streams in Category D require little fuel, and capital charges account for about 43 percent of the total annualized cost of the typical stream shown in Table 8-10.

TABLE 8-10. TYPICAL EMISSION CONTROL COSTS FOR EACH DESIGN CATEGORY[d]

Category	Typical Heating Value (MJ/scm)	Typical Flowrate (MJ/scm)	Installed Capital ($1,000)	Capital Charges ($1,000/yr)	Maintenance ($1,000/yr)	Heat Recovery Credit ($1,000/yr)	Natural Gas Costs ($1,000/yr)	Operating Costs ($1,000/yr)	Annualized Costs ($1,000/yr)
A1	0.69	456	3,900	820	230	3,000	3,400	1,700[b]	2,300
A2	4.2	456	3,900	820	230	3,000	300[a]	-1,400[b]	-(760)
B	0.11	456	1,200	250	71	0	460	630	830
C	1.1	456	780	170	47	0	910	1,040	1,200
D	2.6	456	860	180	52	0	170	290	420
E	4.5	456[c]	1,000	220	63	0	230	370	530

[a] Net energy credit (minus gas costs) of $2,700,000 per year.

[b] Includes $570,000 of caustic costs.

[c] Dilution flowrate of 609 scm/min used in calculating costs.

[d] December, 1978 dollars.

The very rich streams of Category E, which are conservatively assumed to be diluted to avoid exceeding a 980°C combustion temperature, consequently require a larger incinerator volume per normal cubic meter of offgas. For this reason and because of the greater gas expansion at the higher combustion temperature, capital charges account for about 42 percent of the total annualized cost of the typical stream shown in Table 8-10.

The percentage of the total annualized cost due to capital charges increases as offgas flowrate decreases due to economies of scale. In contrast, utilities and operating labor are generally linear functions of flowrate. For a given chemical manufacturing process, flowrate is expected to be roughly proportional to capacity. Therefore, the percentage of total annualized costs due to capital charges is also expected to increase as capacity decreases.

Total annualized costs, as well as each contributing factor to them, are expected to be essentially equal for any two given streams with the same flowrate and heating value, but differing VOC contents. (Such streams would have counterbalancing differences in non-VOC combustibles content.)

Total annualized cost (for nonchlorinated streams) is expected to decrease as heating value increases through Categories B and C, reaching a minimum at the low-heating value end of Category D. Total annualized cost is expected to increase with increasing heating value through Categories D and E, due to greater combustion air and dilution air requirements and gas expansion at higher combustion temperatures. This increase is attributable to increased captial charges. For chlorinated Category A1 streams, total annualized cost decreases with increasing offgas heating value. Annualized costs of Category A2 streams are not expected to be particularly sensitive to variation in offgas heating value. Due to higher capital costs attributable largely to the scrubber, chlorinated streams are in general more costly to control than nonchlorinated ones.

8.1.5.4 Cost-Effectiveness of Control of an Individual Facility

The cost-effectiveness values for a facility are defined as total annualized costs per annual Mg of VOC emissions controlled. The cost-effectiveness is calculated with respect to baseline emissions. Uncontrolled

TABLE 8-11. COST EFFECTIVENESS FOR SELECTED STREAMS OF EACH DESIGN CATEGORY

Category	Characteristics	Net Heating Value (MJ/scm)	VOC Content (Volume Percent)	Non-VOC Combustible Content Volume) Percent)	Offgas Flowrate (scm/min)	Annualized Costs ($1,000/yr)	Annual Emissions (Thousand Mg/yr)	Annual Reduction (Thousand Mg/yr)	Cost Effectiveness ($/Mg)
A1	Typical	0.69	0.3	1.5	456	2,300	1.2	1.1	2,100
A2	Typical	4.2	1.5	9.7	456	-760	5.8	5.6	-140
B	Typical	0.11	0.3	0	456	830	1.2	1.1	740
B	Low VOC Content	0.11	0.04	0.4	456	830	0.15	0.15	5,500
B	Low Flowrate	0.11	0.3	0	90	250	0.23	0.22	1,100
B	High Flowrate[a]	0.11	0.3	0	3,326	4,800	8.4	8.3	580
C	Typical	1.1	0.3	2.7	456	1,200	1.2	1.1	1,100
C	High VOC Content	1.1	1.0	1.2	456	1,100	3.8	3.8	290
D	Typical	2.6	0.5	6.8	456	420	1.9	1.9	220
E	Typical	4.5	0.5	13	456[b]	530	1.9	1.9	280

[a] Requires three equipment units.

[b] Dilution flowrate of 609 scm/min used in calculations.

[c] December, 1978 dollars.

emissions were defined as emissions form the primary absorber vent. The estimated baseline control fraction of 58 percent is derived in Chapter 3 and Appendix F. The cost effectiveness for selected vent streams of all design categories and with various offgas characteristics are given in Table 8-11.

That portion of cost-effectiveness attributable to utilities and operating labor is generally insensitive to variations in offgas flowrate or capacity. In contrast, that portion of cost-effectiveness attributable to capital charges is expected to decrease with increasing flowrate. This effect is illustrated by the three Category B streams in Table 8-11 which vary only in offgas flowrate. However, vent streams with flowrates just large enough to require an additional control system unit will have a correspondingly higher cost-effectiveness. The cost-effectiveness of a Category B stream with a flowrate of 1,420 scm/min (the assumed maximum value) is expected to increase about 8 percent if two equipment units are employed.

Increases in VOC content decrease cost-effectiveness in two ways. If non-VOC combustible content remains constant, heating value will increase with increasing VOC content, and that portion of cost-effectiveness attributable to fuel requirements will in general decrease. Emission reduction is proportional to VOC content. Therefore, cost-effectiveness is inversely proportional to VOC content (apart from the relation of heating value to VOC content). This effect is illustrated in Table 8-11 by the pairs of streams which differ from each other only in VOC content.

Cost-effectiveness has a significant dependence on non-VOC combustible content, although the relation is weaker than that between cost-effectiveness and VOC content. Streams which differ in non-VOC combustible content but not in VOC content must have different heating values. Among vent streams in the statistical profile (discussed in Appendix F), variations in non-VOC combustible content are quite pronounced. Cost-effectiveness generally decreases with an increase in heating value, if the VOC content is constant. However, cost effectiveness is expected to increase with increased heating the boundaries of design Categories B and C, due to the loss of potential heat recovery from the offgas. A cost-effectiveness increase is also expected with increased heating value through the range of Category E, due to the increasing dilution air requirements.

The total resource-effectivenss (TRE) index of a vent stream is defined as the cost-effectiveness of the stream, multiplied by 100, and divided by \$88.66 thousand/Mg. The indexing constant of \$88.66 thousand/Mg corresponds to the highest cost-effectiveness of any stream, in the national profile, with a VOC concentration above the detectable limit. The TRE index is a convenient, dimensionless measure of the total resource burden associated with VOC control at a facility. It is independent of the general inflation rate. However, it does assume fixed relative costs of the various resources, such as carbon steel and natural gas.

The TRE index of a process vent stream can be estimated according to the following equation:

$$TRE = \frac{1}{E_{VOC}} \cdot [(a + b (Q_s^{0.88}) + c (Q_s) + d (Q_s) (H_T) + e (Q_s^{0.88}) (H_T^{0.88}) + f (H_T^{0.88})]$$

where:

TRE = Total resource-effectiveness index value.

Q_s = Vent stream design flowrate (scm/min), at a standard temperature of 20°C.

H_T = Vent stream net heating value (MJ/scm), where the net enthalpy of per mole of offgas is based on combustion at 25°C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20°C, as in the definition of Q_s.

E_{VOC} = VOC emission rate reported in kg/hr measured at full operating flowrate.

a, b, c, d, e, and f are coefficients. The set of coefficients which apply to a process vent stream can be obtained from Table 8-12. These coefficients were obtained by substituting the numeric values for all variables, except offgas flowrate, heating value, and VOC content, in the cost and emissions equations given in Tables 8-5 and 8-9. The resulting equations were substituted into the cost-effectiveness equation given in Table 8-9, which was then indexed to a constant cost-effectiveness value as described above. The TRE index equation simplifies to the six terms shown above. At least two of the equation terms equal zero for

TABLE 8-12. COEFFICIENTS OF THE TOTAL RESOURCE-EFFECTIVENESS (TRE) INDEX EQUATION

A1. FOR CHLORINATED PROCESS VENT STREAMS, IF 0 ≤ NET HEATING VALUE (MJ/scm) ≤ 3.3:

Q_s = Standard Flowrate (scm/min)

	a	b	c	d	e	f
$Q_s < 15$	46.21	0	0.763	-0.325	0	0
$15 < Q_s \leq 790$	38.98	0.754	0.763	-0.325	0	0
$790 < Q_s \leq 1590$	77.96	0.819	0.763	-0.325	0	0
$1590 < Q_s \leq 2380$	116.9	0.860	0.763	-0.325	0	0
$2380 < Q_s \leq 3160$	155.9	0.890	0.763	-0.325	0	0
$3160 < Q_s \leq 3960$	194.9	0.915	0.763	-0.325	0	0

A2. FOR CHLORINATED PROCESS VENT STREAMS, IF 3.3 < NET HEATING VALUE (MJ/scm):

Q_s = Standard Flowrate (scm/min)

	a	b	c	d	e	f
$Q_s < 15$	46.21	0	-0.822	0	0	0
$15 < Q_s \leq 790$	38.98	0.754	-0.822	0	0	0
$790 < Q_s \leq 1590$	77.96	0.819	-0.822	0	0	0
$1590 < Q_s \leq 2380$	116.9	0.860	-0.822	0	0	0
$2380 < Q_s \leq 3160$	155.9	0.890	-0.822	0	0	0
$3160 < Q_s \leq 3960$	194.9	0.915	-0.822	0	0	0

B. FOR NONCHLORINATED PROCESS VENT STREAMS, IF 0 ≤ NET HEATING VALUE (MJ/scm) ≤ 0.45:

Q_s = Standard Flowrate (scm/min)

	a	b	c	d	e	f
$Q_s < 15$	18.03	0	0.257	-0.426	0	0
$15 < Q_s \leq 1520$	15.83	0.229	0.257	-0.426	0	0
$1520 < Q_s \leq 3050$	31.66	0.248	0.257	-0.426	0	0
$3050 < Q_s \leq 4570$	47.49	0.262	0.257	-0.426	0	0

C. FOR NONCHLORINATED PROCESS VENT STREAMS, IF 0.45 < NET HEATING VALUE (MJ/scm) ≤ 1.8:

Q_s = Standard Flowrate (scm/min)

	a	b	c	d	e	f
$Q_s < 15$	18.05	0	0.912	-0.403	0	0
$15 < Q_s \leq 1520$	16.86	0.123	0.912	-0.403	0	0
$1520 < Q_s \leq 3050$	33.72	0.134	0.912	-0.403	0	0
$3050 < Q_s \leq 4570$	50.58	0.279	0.912	-0.403	0	0

D. FOR NONCHLORINATED PROCESS VENT STREAMS, IF 1.8 < NET HEATING VALUE (MJ/scm) ≤ 3.4:

Q_s = Standard Flowrate (scm/min)

	a	b	c	d	e	f
$Q_s < 15$	14.31	0	0.073	0	0	0
$15 < Q_s \leq 1340$	12.83	0.154	0.073	0	0	0
$1340 < Q_s \leq 2680$	25.66	0.167	0.073	0	0	0
$2680 < Q_s \leq 4020$	38.49	0.176	0.073	0	0	0

E. FOR NONCHLORINATED PROCESS VENT STREAMS, IF 3.4 < NET HEATING VALUE (MJ/scm):

Q_s = Standard Flowrate (scm/min)

	a	b	c	d	e	f
$Q_s < 15$	14.31	0	0	0.019	0	0.450
$15 < Q_s \leq 1340$	12.83	0	0	0.019	0.047	0
$1340 < Q_s \leq 2680$	25.66	0	0	0.019	0.051	0
$2680 < Q_s \leq 4020$	38.49	0	0	0.019	0.054	0

vent streams in any design category. The term in the gas use equation proportional to squared heating value is sufficiently insignificant that it was ignored in constructing the simplified equation given above and table of coefficients (Table 8-12).

Table 8-12 is divided into the six design categories for control equipment. Under each design category listed in the table, there are several intervals of offgas flowrate. Each flowrate interval is associated with a different set of TRE equation coefficients. The first flowrate interval in each design category applies to vent streams with a flowrate smaller than that corresponding to the smallest control equipment system easily available without special custom design. The remaining flowrate intervals in each design category apply to vent streams which would be expected to use one, two, three, four, or five sets of control equipment, respectively.

8.1.6 Modified/Reconstructed Facilities

As discussed in Chapter 5, few modifications or reconstructions are anticipated for the air oxidation industry. Thus, the costs of control systems for modified/reconstructed facilities will have a minimal impact on the air oxidation industry. No costs for modified/reconstructed facilities were incorporated into the regulatory alternative impact estimates.

However, if a modification or reconstruction were to occur, the cost for installing a control system in an existing plant that has been modified or reconstructed is generally greater than the cost of installing the control system in a new facility with the same exhaust gas parameters. Such additional cost might be due to a steel or concrete deck for the equipment, extra circuit breakers, and extra ducting. Installation labor costs would also be higher for a retrofit situation. In order to reflect the additional installation costs due to retrofit, a retrofit correction ratio of 1.625 was employed. This correction factor is mutliplied by the new source total installed capital cost of a control system to give the retrofit total installed capital cost. The retrofit correction factor is derived in Appendix G.

8.1.7 Regulatory Alternative Impacts

As discussed in Chapter 6, each regulatory alternative would specify a level of national VOC emission reduction from the baseline. It was assumed that the particular facilities required to control emissions under a given regulatory alternative would be those with the lowest projected annualized cost of control, per unit of VOC destroyed. Therefore, in order to project the regulatory alternative impacts, the data vectors in the national profile were ranked in order of increasing estimated cost-effectiveness of VOC emission control by thermal oxidation.

Alternative 0 represents the baseline level of control. Alternatives I through VI would require approximately 31, 46, 57, 66, 81, and 98 percent national VOC reduction, respectively, from the baseline level. These alternatives are based on the use of a thermal oxidizer operated at 871°C (1600°F) with a chamber residence time of 0.75 second to achieve 98 percent VOC control at air oxidation facilities required to incinerate waste stream VOC.

Only a part of all air oxidation facilities would be required to control emissions to achieve the national VOC reduction over the baseline level specified under each regulatory alternative. The percentage of all facilities covered by the air oxidation NSPS that would actually be required to control emissions to 98 percent or 20 ppmv ranges from approximately 7 percent for Alternative I to 100 percent for Alternative VI.

Both capital and annualized operating costs were used to determine total national costs for each regulatory alternative. These national impacts are summarized in Table 8-13. The costs are given in December, 1978 dollars. The fifth year total national annualized cost would increase from $3 million per year for Alternative I to $67 million per year for Alternative VI. The fifth year total national installed capital cost would increase from $6.1 million for Alternative I to $87 million for Alternative VI.

8.1.8 Chemical Process-Specific Costs

Costs for each specific chemical manufacturing process were developed for use in the economic analysis presented in Chapter 9. Capital, annualized, operating, and control costs (cents per kg of product), and TRE values, for each chemical process are given in Table 8-14 in December, 1978 dollars.

TABLE 8-13. SUMMARY OF ENVIRONMENTAL, ENERGY AND ECONOMIC IMPACTS OF EACH REGULATORY ALTERNATIVE

Regulatory Alternative	Cutoff TRE Index	Cutoff Cost Effectiveness[a] ($/Mg)	Percent of Sources Affected	National Emissions (1000 Mg/yr)	Nominal Percent Emissions Reduction Over Baseline	National Energy Impact Million MJ/yr (BBl oil/day)	National Annualized Cost Million $/yr)	Cost Effectiveness ($/Mg)	Cost Effectiveness (Marginal to Previous Alternative) ($/Mg)	National Capital Cost (Million $)
Baseline	-	-	0	22	0	0 (0)	0	-	-	0
I	.74	660	7	15	31	230 (110)	3.0	450	450	6.1
II	1.5	1,300	14	12	46	520 (240)	7.0	680	1,200	13
III	2.2	1,900	19	9.4	57	770 (360)	10.3[b]	830	1,400	18
IV	3.1	2,700	27	7.5	66	1,000 (460)	15	1,000	2,200	26
V	6.2	5,500	47	4.3	81	2,400 (1,100)	28	1,600	4,000	42
VI	6,000	5,400,000	100	0.44	98	6,000 (2,800)	67	3,100	15,500	87

[a] Highest projected cost-effectiveness of any facility projected to reduce emissions by 98 percent under the given regulatory alternative. This cutoff cost-effectiveness for a facility is calculated with respect to baseline emissions.

[b] In order to give a conservative estimate of accumulated costs, this value was rounded up to $11 Million/yr in Chapter 9 and as the basis for calculations in Section 8.2.1.

Uncontrolled Emissions = 78,000 Mg/yr

Baseline Emissions = 22,000 Mg/yr

TABLE 8-14. CHEMICAL PROCESS-SPECIFIC COSTS

Chemical (Process)[a]	Capital Cost ($1,000/yr)	Annualized Cost ($1,000/yr)	Operating Cost ($1,000/yr)	Control Cost (Cents/kg)	Projected TRE Value[c]
Acetaldehyde	2400	2100	1700	1.8	11
Acetic Acid (Wacker)	1100	680	500	2.8[b]	0.9
Acetic Acid (Butane)	4400	3700	3100	1.5	2.0
Formic Acid	4400	3700	3100	1.5	2.0
Methyl Ethyl Ketone	4400	3700	3100	1.5	2.0
Propionic Acid	4400	3700	3100	1.5	2.0
Acetone (Cumene)	480	240	170	0.9	0.9
Acetophenone	480	240	170	0.9	0.9
Cumene Hydroperoxide	480	240	170	0.7	0.9
Methyl Styrene	480	240	170	0.7	0.9
Phenol	480	240	170	0.7	0.9
Acrylic Acid	1300	1400	1200	2.0	0.1
Acrolein	1300	1400	1200	2.0	0.1
Acrylonitrile (Propene)	4600	1700	990	1.5	0.1
Acetonitrile	4600	1700	990	1.5	0.1
Hydrogen Cyanide	4600	1700	990	1.5	0.1
Anthraquinone	430	210	150	15.2	79
Benzaldehyde	280	84	41	9.0	42
Benzoic Acid	330	120	73	4.4	17
1,3-Butadiene	1800	860	580	4.0	11
p-t-Butyl Benzoic Acid	280	84	41	4.0	21
n-Butyric Acid	360	150	94	3.1	53
Crotonic Acid	300	110	63	2.4	13
Cyclohexanol	740	260	140	0.7	0.2
Cyclohexanone	740	260	140	0.7	0.2
Dimethyl Terephthalate	2700	2200	1800	1.3	1.1
Terephthalic Acid	2700	2200	1800	1.3	1.1
Ethylene Oxide	1100	460	300	1.1	0.2
Formaldehyde (Metal Oxide)	350	130	77	2.9	2.7
Formaldehyde (Silver)	280	-(71)	-(114)	-(1.1)	-(1.4)
Glyoxal	290	100	56	9.5	50
Hydrogen Cyanide	280	-(40)	-(82)	-(6.0)	-(4.8)
Isobutyric Acid	290	130	84	3.8	0.6
Isophthalic Acid	2600	1700	1300	2.9	1.6
Maleic Anhydride (Benzene)	1000	440	280	5.3	0.5
Maleic Anhydride (Butane)	2100	730	410	4.0	1.8
Phthalic Anhydride (Xylene)	1200	580	390	4.6	0.5
Phthalic Anhydride (Naphthalene)	1300	860	660	2.9	0.9
Propionic Acid (Propionaldehyde)	440	240	180	0.7	0.5
Propylene Oxide (Ethylbenzene)	5200	4800	4000	0.9	17.5
Styrene	5200	4800	4000	0.9	17.5
Ethylene Dichloride	1700	-(63)	-(310)	0.2	-(0.1)

[a] Chemicals that are coproducts or byproducts of a particular air oxidation process are indented.

[b] 1.1 kg of acetaldehyde is used to produce 1 kg of acetic acid in the Wacker process. Hence 1.1 x control cost of acetaldehyde is added to the control cost of acetic acid (Wacker process).

[c] These TRE values are for typical facilities. The TRE values for actual facilities would, in general, be different.

Several of these processes produce by-products and/or co-products. For such processes, the by-products and co-products are listed under the main product in Table 8-14. A single value of capital cost, annualized cost, and operating cost was projected for such processes. In calculating the control costs (cents per kg of product) for by-products and co-products, the total annualized cost for the process was attributed to each by-product/co-product. Likewise, the total production of all by-products and co-products was used in calculating the control cost of each by-product/co-product. Therefore, the control costs of the by-product(s)/co-product(s) are equal. This method of projecting control costs is equivalent to sharing the total annualized cost of the process by weight of product.

The method of calculating chemical process-specific costs differed from the methods used elsewhere in this chapter in several respects. These differences, as well as parameters of the individual processes, are discussed in detail in Appendix G. For those processes employing a vapor-phase air oxidation reaction (discussed in Chapter 3), offgas flowrates were predicted according to the method discussed in Appendix F. An after-tax discount rate of 8.5 percent was used. The actual offgas oxygen concentrations were considered in estimating offgas flowrates and capital costs. Chemical processes with offgas net heating values that fall in Categories D and E were assumed to have a heat recovery credit due to use of a waste heat boiler. No dilution of offgas was assumed for processes with heating values within the Category E range. For processes with heating values within the range of Category C, offgas dilution sufficient to permit use of 70 percent recuperative heat recovery was assumed, if such dilution would result in lower projected annualized costs. Such processes were assumed to employ an offgas dilution sufficient to yield a net heating value of 0.48 MJ/Nm^3, and place the process within design Category B.

8.2 OTHER COST CONSIDERATIONS

8.2.1 Control Cost Accumulation for Synthetic Organic Chemical Manufacturing Industries Using Air Oxidation Processes

8.2.1.1 Introduction

Since passage of the Clean Air Act Amendments of 1977, EPA has initiated action on eight possible new source performance and hazardous air pollutant standards that will affect the air oxidation industry.

None has been promulgated as of the proposal date of the air oxidation standard. The adjusted accumulated fifth-year annualized cost of these potential regulations is $21.1 million. The air oxidation standard comprises $11 million (52 percent) of the total cost resulting from these potential regulations. About one-half of this cost will be borne by the air oxidation industry and its customers and suppliers. The other half will be paid by the taxpayers in the form of foregone tax revenues. This cost is judged to be reasonable.

It is necessary that the air oxidation industry be defined in precise terms before the costs of regulations can be identified and accumulated. The air oxidation industry, as the term is used in this discussion, consists of all facilities and activities directly involved in the production, or storage prior to shipment, of any of 26 air oxidation chemicals regardless of whether the production is by an air oxidation process. This definition is broad in the sense that it includes a large number of facilities that produce air oxidation chemicals by nonair-oxidation processes, as well as many existing facilities that will not be affected by a possible air oxidation standard. However, the definition excludes facilities for the production of nonair-oxidation chemicals by the same firms that produce air oxidation chemicals, facilities for the production of about 10 air oxidation chemicals that are very low volume chemicals or that have no projected growth, and terminal storage of air oxidation chemicals away from the production site. Despite these shortcomings, the definition is sufficiently broad so that cost projections will be conservative (higher than the actual costs).

Listed below are the relevant potential regulations for cumulative costs with corresponding Start Action Notice (SAN) numbers:

1. NESHAP: Benzene Emissions from Benzene Storage Tanks, SAN No. 1593.
2. NESHAP: Benzene Fugitive Emissions, SAN No. 1126.
3. NESHAP: Benzene Emissions from the Ethylbenzene/Styrene Industry, SAN No. 1128.
4. NESHAP: Benzene Emissions from the Maleic Anhydride Industry, SAN No. 1127.
5. NSPS: VOC Fugitive Emissions in Synthetic Organic Chemicals Manufacturing Industry, SAN No. 1112.

6. NSPS: VOC Emissions from Volatile Organic Liquid Storage Tanks, SAN No. 1612.

7. NSPS: VOC Emissions from Air Oxidation Process Vents in the Synthetic Organic Chemical Manufacturing Industry, SAN No. 1618.

8. NSPS: VOC Emissions from Distillation Process Vents in the Synthetic Organic Chemical Manufacturing Industry. (No SAN has been issued at this time.)

The basic methodology employed to generate cumulative annualized control costs is presented below:

1. All control costs are standardized to mid-1978 dollars.

2. All control costs are annualized using a real, before-tax interest rate of 10 percent.

3. Only the EPA Administrator's recommended regulatory alternative is considered when accumulating costs for existing (NESHAP's) and new, modified, or reconstructed (NESHAP's and NSPS's) facilities. In cases where development of a regulation has not progressed to a late enough stage to have a recommended regulatory alternative, a best estimate is made of the most likely regulatory alternative to be selected.

4. All control costs are incremental and do not include the cost of pollution control equipment already in place.

5. Costs are tabulated only for the specific chemical industries that make up the air oxidation industry and are thus directly affected by the potential air oxidation process NSPS. For example, the potential VOC Fugitive Emissions NSPS affects a far greater number of chemical industries than does the potential air oxidation process NSPS, but the annualized costs of control of the potential VOC Fugitive Emissions NSPS are calculated only for the chemical industries that utilize the air oxidation process.

6. For NESHAP and NSPS regulations, the fifth year total annualized control costs for new, modified, or reconstructed facilities are used for accumulation. The fifth year total annualized control costs refer to the control costs expected to be incurred by the affected industry, customers, and suppliers in the fifth year following proposal of a standard in the FEDERAL REGISTER. The fifth year costs are calculated by multiplying annualized control costs for one facility (in constant dollars) by the projected number of facilities to be affected by the

regulation. The fifth year will vary among potential regulations because the dates of proposal in the FEDERAL REGISTER vary among potential regulations. The number of new facilities using the air oxidation process expected to be built between December 1, 1981 and December 1, 1986 (see Table 9-11, Scenario I) is used to calculate fifth year control costs for all four of the potential NSPS regulations, even though the five year period used for air oxidation projections does not correspond exactly to five year periods of other regulations.

7. When costs are accumulated, a few individual chemical industries for which projections are made can be grouped together as one industry because of the existence of coproducts or byproducts. To avoid any double counting when projecting the number of new facilities, coproducts are combined as one industry (e.g., propylene oxide is combined with styrene, terephthalic acid is combined with dimethyl terephthalate, acetic acid is included with methyl ethyl ketone, acrylonitrile is combined with hydrogen cyanide, and acetone is included with phenol). Byproducts are included with their primary product as one industry (i.e., n-butyric acid, formic acid, and propionic acid are included with acetic acid and methyl ethyl ketone; acetophenone, cumene hydroperoxide, and α-methyl styrene are included with acetone and phenol; acetonitrile is included with acrylonitrile and hydrogen cyanide; and acrolein is combined with acrylic acid). Refer to Section 9.1.8 and Section 3.3.1 for more information on coproducts and byproducts.

8. Table 9-11 gives a projection only for future facilities using the air oxidation process. Some of the chemical industries using an air oxidation process will also utilize nonair-oxidation processes. Cumulative costing here involves the entire industry so when deriving control costs for the VOC fugitive emissions, volatile organic liquid storage tanks and distillation columns NSPS's, both air oxidation and nonair-oxidation process facilities are examined. In order to project the total number of facilities for each industry, the projected number of new air oxidation facilities, as reported in Table 9-11, is divided by the ratio of estimated production by an air oxidation process to total production by all processes in 1982 for each of 17 industries (the projections in Table 9-11 are rounded off; in this excercise the unrounded projection calculations are used). These ratios are presented in percentage terms in Table 3-7. The results of this exercise are found on Table 8-15.

TABLE 8-15. FIVE YEAR PROJECTIONS OF NEW FACILITIES UTILIZING BOTH AIR OXIDATION AND NONAIR-OXIDATION PROCESSES

Chemical[a]	Number of New Facilities
Acetaldehyde	3
Acetic acid	2
n-Butyric acid Formic acid Methyl ethyl ketone Propionic acid[b]	
Acetone	4
Acetophenone Cumene hydroperoxide α-Methyl styrene Phenol	
Acrylic acid	1
Acrolein	
Acrylonitrile	0
Acetonitrile Hydrogen cyanide[c]	
Benzoic acid	3
1,3-Butadiene	6
Ethylene dichloride	5
Ethylene oxide	1
Formaldehyde	19
Hydrogen cyanide[c]	4
Isophthalic acid	1
Maleic anhydride	6
Phthalic anhydride	3
Propionic acid[b]	0
Propylene oxide[d]	2
Styrene	
Terephthalic acid	1
Dimethyl terephthalate	

[a] Chemicals that are coproducts or byproducts of a particular air oxidation process are indented. The projected number of new facilities producing these chemicals is zero to avoid double counting. Refer to Section 9.1.8 for more information on coproducts and byproducts.

[b] When produced by the propionaldehyde oxidation process, propionic acid is an only product, but is a byproduct when produced with acetic acid, n-butyric acid, formic acid, and methyl ethyl ketone (n-butane oxidation process).

[c] Hydrogen cyanide is principally produced as an only product but is also produced in the propylene ammoxidation process as a coproduct with acrylonitrile.

[d] One of the two projected new facilities will utilize an air oxidation process, and in this case propylene oxide and styrene are coproducts. The other projected facility will produce only styrene (a nonair-oxidation process) but is placed with propylene oxide to be consistent and avoid confusion. The cost calculations are not affected.

9. Table 8-16 lists the costs for 26 of the 36 chemical industries affected by the potential air oxidation process NSPS. Two chemical industries, acrylonitrile and propionic acid (propionadehyde oxidation process), have zero new, modified, or reconstructed facilities projected and hence do not experience any NSPS costs. The other eight chemical industries are excluded for lack of information needed to project new facilities. However, the eight chemical industries omitted represent only five percent of the total air oxidation process capacity.

The data presented in Table 8-16 are based on the above general methodology and more specific assumptions. These regulation-specific assumptions are presented below.

8.2.1.2 Data and Assumptions for Accumulating Costs

1. Benzene Storage NESHAP. Cost data are from the draft Environmental Impact Statement (EIS) titled "Benzene Emissions from Benzene Storage Tanks -- Background Information for Proposed Standards," December 1980, (EPA-450/3-80-034a). Page numbers referencing costs are from this EIS.

Cost data in the EIS are in first quarter 1979 dollars.

The benzene storage NESHAP would affect two chemical industries that utilize the air oxidation process: maleic anhydride and styrene. Both of these industries are benzene consumers.

EPA recommends (45 FR 83952) regulatory alternative IV for existing sources and regulatory alternative III for new sources. Alternative IV requires that each fixed roof, external floating roof, and internal floating roof tank be converted to a contact internal floating roof tank with a liquid-mounted primary seal and a continuous secondary seal. Alternative III requires that each fixed roof, external floating roof, and internal floating roof storage tank be converted to a contact internal floating roof tank with a liquid-mounted primary seal.

The cost to existing styrene and maleic anhydride facilities is $6,800 per facility (p. 7-45) for Alternative IV. There are 12 styrene facilities and 10 maleic anhydride facilities presently in existence (see Table 9-1). Hence, the total cost to all existing styrene and maleic anhydride facilities is $81,600 and $68,000, respectively.

The control cost for new styrene and maleic anhydride facilities is $5,700 per facility (p. 7-53) for Alternative III. According to Table 8-15, six new facilities are projected for maleic anhydride.

TABLE 8-16. TOTAL FIFTH YEAR ANNUALIZED COST OF CONTROL FOR EACH CHEMICAL INDUSTRY THAT UTILIZES THE AIR OXIDATION PROCESS, ACCUMULATED BY POTENTIAL AIR REGULATIONS

26 Chemical Industries
United States
1978

(Costs are in Mid-1978 $ and Rounded to the Nearest 1,000)

Chemical Industry[b]	Benzene Storage NESHAP	Benzene Fugitives NESHAP	Ethylbenzene/ Styrene NESHAP	Maleic Anhydride NESHAP	VOC Fugitive Emissions NSPS	Volatile Organic Liquid Storage Tanks NSPS	Air Oxidation Processes NSPS	Distillation Columns NSPS	Total
Acetaldehyde	X	X	X	X	39,000	-21,000	0	170,100	188,100
Acetic acid n-Butyric acid[c] Formic acid[c] Methyl ethyl ketone[c] Propionic acid[c]	X	X	X	X	26,000	-14,000	2,057,000	113,400	2,182,400
Acetone Acetophenone[c] Cumene hydroperoxide[c] α-Methyl styrene[c] Phenol	X	X	X	X	52,000	-28,000	220,000	226,800	470,800
Acrylic acid Acrolein[c]	X	X	X	X	13,000	-7,000	781,000	56,700	843,700
Benzoic acid	X	X	X	X	39,000	-21,000	176,000	170,100	364,100
1,3-Butadiene	X	X	X	X	78,000	-43,000	418,000	340,200	793,200
Ethylene dichloride	X	X	X	X	65,000	-36,000	0	283,500	312,500
Ethylene oxide	X	X	X	X	13,000	-7,000	275,000	56,700	337,700
Formaldehyde	X	X	X	X	247,000	-135,000	308,000	1,077,300	1,497,300
Hydrogen cyanide	X	X	X	X	52,000	-28,000	33,000	226,800	283,800
Isophthalic acid	X	X	X	X	13,000	-7,000	781,000	56,700	843,700
Maleic anhydride	63,000	78,000	X	1,885,000	78,000	-43,000	1,661,000	340,200	4,062,200
Phthalic anhydride	X	X	X	X	39,000	-21,000	1,001,000	170,100	1,189,100
Propylene oxide Styrene[c]	86,000	127,000	4,078,000	X	26,000	-14,000	2,255,000	113,400	6,671,400
Terephthalic acid Dimethyl terephthalate[c]	X	X	X	X	13,000	-7,000	1,034,000	56,700	1,096,700
	149,000	205,000	4,078,000	1,885,000	793,000	-432,000	11,000,000	3,458,700	21,136,700

[a] The fifth year varies among standards. Refer to pg. 8-33, #6 for further explanation.

[b] Only 26 of the 36 chemical industries affected by the air oxidation processes NSPS are listed. Refer to pg. 8-35, #9 for further explanation.

[c] These chemicals are coproducts or byproducts of a particular air oxidation process. For further explanation refer to pg. 8-34, #7.

NOTE: 1) Derivation of each regulation's annualized control cost is provided in the following pages.
2) "X" denotes that these chemical industries are not covered by the particular standard.

However, it is believed that all new maleic anhydride sources will use n-butane instead of benzene as the main feedstock. Hence, benzene storage costs will be zero for future maleic anhydride facilities. Two styrene facilities are projected to be constructed, one producing styrene as a coproduct with propylene oxide by an air oxidation process and the other producing styrene by a nonair-oxidation process. Total annualized cost of control for new styrene sources is $11,400.

An aggregation of control costs for existing and new sources amounts to $93,000 for the styrene industry and $68,000 for the maleic anhydride industry. The mid-1978 producer's price index is 209.6 and the first quarter 1979 producer's price index is 226.7. In mid-1978 dollars, the total annualized cost of control is $86,000 for the styrene/propylene oxide industry and $63,000 for the maleic anhydride industry.

2. Benzene Fugitives NESHAP. Cost data are from the draft EIS titled "Benzene Fugitive Emissions-Background Information for Proposed Standards," November 1980, (EPA-450/3-80-032a). Page numbers referencing costs are from this EIS.

Cost data in the EIS are in May 1979 dollars.

The benzene fugitive NESHAP would affect two chemical industries that utilize the air oxidation process: maleic anhydride and styrene. Both of these industries experience fugitive benzene emissions.

EPA recommends (46 FR 1165) regulatory Alternative III for existing sources. Regulatory Alternative III requires the installation of closed-loop sampling systems and rupture disks on gas service safety/relief values that vent to the atmosphere. Degassing vents on pump seal oil reservoirs would be required to be vented to a closed system; accumulator vessels would be required to be vented to a closed system; and open-ended valves would be required to be sealed with a cap, blind, plug, or another valve. Monthly monitoring for detection of leaks from pumps, drain compressors, and valves would also be required. Regulatory Alternative IV requires double seals on pumps and compressors in addition to the requirements of regulatory Alternative III. EPA recommends that Alternative IV be imposed in the case of new sources.

The cost to existing styrene and maleic anhydride facilities is $8,700 per facility when Alternative III is imposed. This number is derived from the control costs for three different model facilities.

The cost of control for model facility A is $7,400, for model facility B, $9,700, and for model facility C, $15,200 (pp. 8-26 through 8-31). It is estimated that 62 percent of existing refinery and SOCMI benzene-related production units would be represented by model A, 31 percent by model B, and seven percent by model C (p. 6-3). The $8,700 per facility cost is an average control cost for the three model facilities, weighted by the estimated current population of each model facility. There are 12 styrene facilities and 10 maleic anhydride facilities presently in existence (see Table 9-1). Hence, the total cost to all existing styrene and maleic anhydride facilities is $104,400 and $87,000, respectively.

The control cost for new styrene and maleic anhydride facilities is $18,200 per facility when Alternative IV is imposed. This figure is based on the same model facilities used for existing sources. The cost of control for a new model facility A is $12,000, for new model facility B is $25,700, and for new model facility C is $39,900. Because it is expected that new facilities will follow the same distribution as the current population, the weighting procedure (i.e., model A-62 percent, model B-31 percent, model C-7 percent) is implemented to determine the composite cost. The should be no new maleic anhydride sources using benzene, so there is no cost. Two styrene facilities (one producing styrene as a coproduct with propylene oxide by an air oxidation process, the other producing styrene by a nonair-oxidation process) are projected to be constructed (refer to air oxidation BID page 8-34, #8). Total annualized cost of control for new styrene sources is expected to be $36,400.

Aggregate control costs for existing and new sources amount to $140,800 for the styrene industry and $87,000 for the maleic anhydride industry. The mid-1978 producer's price index is 209.6 and the May 1979 producer's price index is 232.0. In mid-1978 dollars the total annualized cost of control is $127,000 for the styrene industry and $78,000 for the maleic anhydride industry.

3. Ethylbenzene/Styrene NESHAP. Cost data are from the draft EIS titled "Benzene Emissions from Ethylbenzene/Styrene Industry-Background Information for Proposed Standards," August 1980, (EPA-450/3-79-035a). Page numbers referencing costs are from this EIS.

Cost data in the EIS are in fourth quarter 1978 dollars.

The ethylbenzene/styrene NESHAP would affect one chemical industry that utilizes the air oxidation process: styrene.

EPA recommends (45 FR 83448) regulatory Alternative C for continuous emissions and regulatory Alternative I for excess emissions. Alternative C requires that facilities achieve 99 percent benzene emission reduction in the main process vents based on the use of a boiler or process heater. Alternative I would require the use of smokeless flares. Most styrene facilities have flares in place and only four existing facilities would be required to install smokeless flares.

The cost to an existing styrene facility is $400,000 if a flare (Alternative I) is needed, and $229,000 if a flare is presently in place. The annualized cost per facility to control continuous emissions is a $460,000 credit (p. 7-41). The analysis assumed that benzene is recovered in the condenser and scrubber system and is fed back into the process via the benzene drying column. The value of the benzene recovered is subtracted from the control cost. In this case the value of the benzene recovered is greater than the control cost. The cost of controlling excess emissions is $171,000 per plant and the cost of monitoring is $689,000. Multiplying the $400,000 cost by the four plants that do not have flares in place results in a $1,600,000 cost. The other eight existing styrene plants experience an aggregate cost of $1,832,000 ($229,000 times eight). Thus, the total control cost to existing styrene facilities is $3,432,000.

The EIS did not project any new styrene facilities, so costs were not derived for new sources. It is assumed that new sources producing styrene will experience the $400,000 control cost. Two styrene facilities (one producing styrene as a coproduct with propylene oxide by an air oxidation process and the other producing styrene by a nonair oxidation process) are projected to be constructed (refer to Table 8-15). The total annualized cost of control for new styrene sources is $800,000.

Aggregate control costs for existing and new sources amount to $4,232,000 for the styrene industry. The mid-1978 producer's price index is 209.6 and the fourth quarter 1978 producer's price index is 217.5. In mid-1978 dollars the total annualized cost of control for the styrene/propylene oxide industry is $4,078,000.

4. Maleic Anhydride NESHAP. Cost data are from the draft EIS titled "Benzene Emissions from the Maleic Anhydride Industry-Background Information for Proposed Standards," February 1980, (EPA-450/3-80-001a). Page numbers referencing costs are from this EIS.

Cost data in the EIS are in second quarter 1979 dollars.

This regulation would affect only the maleic anhydride industry.

EPA recommends (42 FR 26660) a 97 percent efficiency control option for existing sources. For the 97 percent regulatory option, the total annualized control costs would be approximately $2,100,000 for the existing maleic anhydride industry (p. 5-63). The mid-1978 producer's price index is 209.6 and the second quarter 1979 producer's price index is 233.5. In mid-1978 dollars the total annualized cost of control is $1,885,000 for the maleic anhydride industry.

5. VOC Fugitive Emissions NSPS. Cost data are from the draft EIS titled "VOC Fugitive Emissions in Synthetic Organic Chemicals Manufacturing Industry - Background Information for Proposed Standards," November 1980, (EPA-450/3-80-033a). Page numbers referencing costs are from this EIS.

Cost data in the EIS are in fourth quarter 1978 dollars.

The VOC fugitive emissions NSPS would affect all SOCMI chemicals that are produced using the air oxidation process.

EPA recommends (46 FR 1136) regulatory Alternative IV. Alternative IV requires: a) the monthly monitoring of all in-line valves and open-ended valves in gas and light liquid service, b) the installation of rupture discs upstream of service safety/relief valves that vent to the atmosphere, c) the installation of closed vents and control devices for compressor seal areas and/or degassing vents from compressor barrier flued reservoirs, d) the installation of dual mechanical seals on pumps in light liquid service and installation of closed vent control devices for degassing vents from barrier fluid reservoirs of all pumps in light liquid service, e) the installation of closed loop sampling systems, and f) the installation of caps, blinds, plugs, or second valves to seal all open-ended lines.

The cost of this standard is $13,500 per facility if Alternative IV is used. This figure is derived from the control costs for three different model facilities. The cost of control for model facility A is $7,900, for model facility B, $13,300, and for model facility C, $33,000 (pp. 8-14 through 8-16). The EIS estimates that 52 percent of existing SOCMI plants are similar to model facility A, 33 percent are similar to B, and 15 percent are similar to C (p. 6-2). It is assumed that this distribution will hold for the future SOCMI facility population. The $13,500 per facility cost is an average control for the three model facilities, weighted by the estimated current SOCMI population of each model facility.

To arrive at specific chemical industry costs, the $13,500 per facility control cost is multipled by the projected number of new sources for each chemical industry that uses air oxidation processes (refer to Table 8-15). All costs are multiplied by 209.6/217.5, the ratio of the mid-1978 producer's price index to the fourth quarter 1978 producer's price index, in order to put all costs in mid-1978 dollars.

6. Volatile Organic Liquid Storage Tanks NSPS. Cost data are from the draft EIS titled "VOC Emissions from Volatile Organic Liquid Storage Tanks - Background Information for Proposed Standards," April 1981, (EPA-450/3-81-003a). Page numbers referencing costs are from this EIS.

Cost data in the EIS are in first quarter 1980 dollars.

The Volatile Organic Liquid Storage Tanks NSPS would affect all SOCMI chemicals that are produced using the air oxidation process.

As stated in the preamble of the EIS, EPA recommends regulatory Alternative IV. This option would require that each storage vessel storing a VOL with a true vapor pressure less than 76.6 kPa be equipped with a contact internal floating roof with a liquid-mounted primary seal and a continuous secondary seal. A vapor control system would be required for all storage vessels storing a VOC with a true vapor pressure greater than or equal to 76.6 kPa.

The total annualized cost of regulatory Alternative IV for all of the SOCMI is assumed to be a credit of $5,790,000 (p. 9-48). Product recovery credits are assumed to be 36¢/kg, the average value of recovered products. In order to obtain specific chemical industry costs the $5,790,000 figure is divided by the total storage tank population of 47,059 (p. 9-47). This calculation gives a credit of $123 per storage tank. The $123 is multiplied by 72, the average number of storage tanks at each facility (p. 9-47). This results in an approximate credit of $9,000 per facility.

To arrive at specific chemical industry credits, the $9,000 credit is multiplied by the projected number of new sources for each chemical industry that uses the air oxidation process (refer to page 8-34, #8 for projections). All credits are multiplied by 209.6/261.5, the ratio of the mid-1978 producer's price index to first quarter 1980 dollars, in order to put all costs in mid-1978 dollars.

7. Air Oxidation Processes NSPS. Cost data are obtained from Chapter 8 of this document and are in mid-1978 dollars.

For purposes of convenience, it is guessed that Regulatory III will be the preferred course of action. This alternative requires a 57 percent national VOC reduction from the baseline level based on the use of a thermal oxidizer at those air oxidation facilities required to meet a 98 percent VOC reduction requirement.

The national annualized cost is estimated to be $11,000,000 when regulatory Alternative III is chosen (Table 8-13 of this BID). It is not possible to determine which future air oxidation facilities would be required to control VOC emissions to achieve the national emission reduction under regulatory Alternative III. In order to accumulate costs on an individual industry basis, it is assumed that the $11,000,000 total cost will be shared based on a specific industry's individual plant costs and projected number of new sources. Table 9-11 of this document provides the projected number of new air oxidation facilities and Table 8-14 gives chemical process-specific costs. For each industry the projected number of new facilities is multiplied by each chemical industry's specific cost. The products are summed to arrive at a total cost for all industries. Next, the percentage of the total cost attributable to each specific industry is calculated and the $11,000,000 national annualized cost of control is distributed to each chemical-specific industry based on these percentages. Table 8-17 presents the calculations and results.

8. Distillation Columns NSPS. Cost data are obtained from the most recent ESED contractor memorandum (June 3, 1981). The cost data obtained are based on worst case assumptions and are in mid-1978 dollars.

The Distillation Columns NSPS would affect all SOCMI chemicals that are produced using the air oxidation process. No regulatory alternatives have been defined as of yet.

TABLE 8-17. FIFTH YEAR ANNUALIZED COSTS OF THE NSPS FOR AIR OXIDATION PROCESS, BY SPECIFIC INDUSTRY

26 Chemical Industries
United States
1978

Chemical Industry	Projected Number of air Oxidation Facilities	Annualized Chemical Process-Specific Costs ($1,000)	Total Projected Cost per Industry: AxB ($',000)	Share of all Industry's Cost: AxB ÷ Sum of Column (C)	Alternative III Costs per Industry: Column D Multiplied by $11,000,000
Acetaldehyde	0	2,083	0	.000	0
Acetic acid n-Butyric acid Formic acid Methyl ethyl ketone Propionic acid	2	2,196[a]	4,392	.187	2,057,000
Acetone Acetophenone Cumene hydroperoxide α-Methyl styrene Phenol	4	240	480	.020	220,000
Acrylic acid Acrolein	1	1,661	1,661	.071	781,000
Benzoic acid	3	122	366	.016	176,000
1,3-Butadiene	1	895	895	.038	418,000
Ethylene dichloride	2	-16	-32	.000	0
Ethylene oxide	1	581	581	.025	275,000
Formaldehyde	19	35[b]	665	.028	308,000
Hydrogen cyanide	4	20	80	.003	33,000
Isophthalic acid	1	1,658	1,658	.071	781,000
Maleic anhydride	6	590[c]	3,540	.151	1,661,000
Phthalic anhydride	3	713[d]	2,139	.091	1,001,000
Propylene oxide Styrene	1	4,816	4,816	.205	2,255,000
Terephthalic acid Dimethyl terephthalate	1	2,213	2,213	.094	1,034,000
Total			23,454	1.000	11,000,000

[a] The number is based on the assumption that one acetic acid projected facility will use the Wacker process and the other the n-butane process.

[b] The number is based on the assumption that 12 of the projected formaldehyde facilities will use a crystalline silver catalyst, methanol, and air in the air oxidation process and seven will use a mixed metal catalyst, methanol, and air in the air oxidation process.

[c] The number is based on the assumption that all future maleic anhydride facilities will use n-butane as a feedstock.

[d] The number is based on the assumption that two of the projected phthalic anhydride facilities will use xylene as a feedstock and one will use naphthalene as a feedstock.

NOTE: These assumptions are based on current facility distributions or future known trends.

The worst case cost (100 percent control) for each facility with distillation columns is $354,100. The regulatory alternative chosen for the air oxidation NSPS represents approximately 16 percent of the cost associated with the air oxidation NSPS regulatory alternative requiring 100 percent control. It is assumed that the control alternative chosen for distillation will be on a similar level as the control alternative for air oxidation processes. Thus $354,100 is reduced by 84 percent to $56,700 per facility.

For each chemical industry, the projected number of new facilities from Table 8-15 is multiplied by $56,700 to approximate the cost per industry of a distillation column NSPS.

8.2.2 Costs of Regulations Other Than NSPS's and NESHAP's

This section summarizes the costs of all other environmental regulations, other than new source performance and hazardous air pollutant standards, impacting SOCMI. Most of these regulations affect the entire synthetic organic chemical industry, not just air oxidation facilities. There also are regulations which are applicable only to a specific chemical within air oxidation. The other regulations SOCMI has to comply with are water pollution control regulations, worker safety regulations, and toxic and hazardous waste regulations. Table 8-18 lists all the provisions and requirements of the regulations applicable to air oxidation facilities. All cost information is in December 1978 dollars.

8.2.2.1 Water Pollution Control Regulations

1. Federal Water Pollution Control Act (FWPCA). SOCMI facilities are required by the FWPCA to comply with effluent limitation guidelines. Under the guidelines for the organic chemicals manufacturing industry, existing sources must apply best practical control technologies available (BPCTA) and new sources must apply best available demonstrated control technology (BADCT).[48] Currently, guidelines for organic chemicals are being revised.

The Clean Water Act of 1977 amended the FWPCA and required that the best available technology economically achievable (BATEA) be implemented by 1984 for non-conventional and toxic pollutants. For conventional pollutants, best conventional technology (BCT) is required. The guidelines developed for BCT take different cost considerations into account than BATEA.[49]

TABLE 8-18. STATUTES THAT MAY BE APPLICABLE TO AIR OXIDATION FACILITIES

Statute	Applicable Regulation or Regulations
Clean Air Act and Amendments	• State implementation plans • National emission standards for hazardous air pollutants • New source performance standards - VOC fugitive emissions - Volatile organic liquid storage • PSD construction permits • Nonattainment construction permits
Clean Water Act (Federal Water Pollution Control Act)	• Effluent limitations guidelines • New source performance standards • Discharge permit (NPDES) • Control of oil spills and discharges • Pretreatment requirements • Monitoring and reporting • Permitting of industrial projects that impinge on wetlands or public waters • Environmental impact statements
Resource Conservation and Recovery Act	• Hazardous wastes - Permits for treatment, storage, and disposal of hazardous wastes - Manifest system to track hazardous wastes - Establishes recordkeeping, reporting, labeling, and monitoring system for hazardous wastes • Nonhazardous wastes - State discharge programs
Toxic Substances Control Act	• Toxicity testing • Premanufacture notification • Labeling, recordkeeping • Reporting requirements
Occupational Safety and Health	• Occupational health and environmental control standards • Hazardous material standards

TABLE 8-18 (Continued). STATUTES THAT MAY BE APPLICABLE TO AIR OXIDATION FACILITIES

Statute	Applicable Regulation or Requirements
Occupational Safety and Health (cont'd)	• General environmental control standard • Personal protective equipment standards • Building safety and health standards (unrelated to product) • Medical and first aid standards • Fire protection standards • Walking-working surface standards • Means of egress standards • Compressed gas and compressed air equipment • Welding, brazing, and cutting standards
Comprehensive Environmental Response, Compensation, and Liability Act (Superfund)	• Cleanup costs for dumpsites and spills • Tax to establish post-closure trust fund
Safe Drinking Water Act	• Primary and secondary drinking water standards for groundwater • Underground injection control permits
Marine Protection, Research, and Sanctuaries Act	• Ocean dumping permits • Recordkeeping and reporting

EPA has developed water quality criteria documents for 64 toxic water pollutants or categories of pollutants. These documents contain recommended maximum permissible pollutant concentrations for the protection of aquatic organisms, human health, and some recreational activities. These documents do not consider treatment technology, costs, or other feasibility factors.[50] The air oxidation chemicals listed as toxic pollutants to be controlled are:

(1) acrolein,
(2) acrylonitrile,
(3) cyanides, and
(4) phenol.

The National Pollution Discharge Elimination System (NPDES) enables States to issue discharge permits. Eighty-five percent of the chemical products industry (SIC 28) is in compliance with the Federal water pollution reporting regulations required under NPDES.[51]

The capital cost to the organic chemical industry of controlling water pollution was $3.4 billion from 1970 through 1977. The cumulative capital costs from 1977 to 1986 are expected to be $2.9 billion. The annual cost for 1977 was $401.6 million and the cumulative costs from 1977 to 1986 are expected to be $6.5 billion.[52]

2. Safe Drinking Water Act (SDWA). The Safe Drinking Water Act requires EPA to establish primary and secondary drinking water standards. Primary regulations are aimed at protecting public health. They establish maximum allowable contaminant levels in drinking water and provide for water supply system operation. Secondary regulations are designed to protect public welfare and control the taste, odor, and appearance of drinking water. The Act also controls underground injection through permitting. In establishing maximum control levels (MCL), the technological and economic feasibility is considered as well as the health effects. Currently, the MCL for VOC in groundwater is being developed; therefore, control costs are unknown.[53] Since there are very few MCLs at this time, States have the option of controlling toxic pollutants when a MCL does not exist.[54]

8.2.2.2 Occupational Safety and Health Regulations

The Occupational Safety and Health Administration (OSHA) is responsible for protecting workers against hazardous materials found in the workplace. There are two types of regulations established by OSHA which affect the air oxidation industry. The first type is general administrate and engineering controls for hazardous substances. The air oxidation chemicals that are controlled by these general standards are listed in Table 8-19.[55] If engineering controls and work practice standards are not feasible to achieve full compliance, protective equipment is to be used.

A second type of regulation has been developed for the more significant hazardous air pollutants. These are comprehensive regulations that establish administrative and engineering controls specific to one pollutant only. As far as air oxidation chemicals are concerned, comprehensive standards have been promulgated for acrylonitrile only.[56]

The average cost of OSHA regulations on the entire chemical industry is estimated to be $208.40 per worker per year.[57] The type of worker protection is dependent on the chemical produced at each air oxidation facility. In those facilities where only general controls are required, the costs would vary with the control method(s) employed by each facility.

OSHA also has specific regulations for chemical facilities which handle, store, or use flammable and combustible liquids with a flash point less than 200°F under Section 29 CFR 1910.106.[58] Once again, OSHA bases these standards on toxicity levels and not on cost criteria.

8.2.2.3 Toxic Substance Control Regulations

Toxic Substance Control Act (TSCA) requirements are based on the need to provide necessary information concerning the toxicity of new and existing chemicals. TSCA requires reporting of the manufacturing, importing, or processing of any chemical substance used for a commercial purpose in order to develop a chemical inventory. Any substance not on the inventory will be considered new and require premanufacture notice and testing. Reporting and premanufacture notification (PMN) includes: (1) the cost of using screening and testing to gain appropriate information for new chemicals, (2) the cost of testing existing chemicals, and (3) the cost of the delay caused by the testing/reporting process. PMN could have a significant impact on the entire chemical industry, with cost estimates ranging from $78.5 million to $2 billion.[59]

Small companies will probably suffer more than the larger firms since small firms have minimal access to the information necessary to develop a PMN. The impact of PMN also will be greater to the small

TABLE 8-19. AIR OXIDATION CHEMICALS REGULATED BY OSHA GENERAL CONTROLS

Acetaldehyde
Acetic Acid
Acetone
Acetonitrile
Acrolein
1,3-Butadiene
Cyclohexanol
Cyclohexanone
Ethylene Dichloride
Ethylene Oxide
Formaldehyde
Formic Acid
Hydrogen Cyanide
Maleic Anhydride
Methyl Ethyl Ketone
α-Methyl Styrene
Phenol
Phthalic Anhydride
Propylene Oxide
Styrene

firms because the cost per product will be higher for low volume, low revenue chemicals. The cost of preparing notices for new chemicals is estimated to be between $820 and $7400 per chemical.[60]

EPA has been concentrating its efforts on new chemicals being developed rather than existing ones; therefore, the actual cost to the SOCMI air oxidation facilities of meeting TSCA is unknown.

8.2.2.4 Solid and Hazardous Waste Regulations

1. Resource Conservation and Recovery Act (RCRA). RCRA establishes a national program to improve solid waste management including the control of hazardous waste, the promotion of resource conservation and recovery, and the establishment of a solid waste disposal program.

The hazardous waste program regulates wastes from generation to disposal ("cradle to grave") requiring EPA to produce standards for generators, transporters, and those who transport, store, and dispose (TSD facilities). The wastes are identified and listed by industry. At the time of generation, a manifest system is developed to record the movement of the wastes from cradle to grave.

The organic chemical industry generates 35 percent of the hazardous wastes generated annually.[61] The air oxidation chemicals listed in Table 8-20 are considered hazardous under RCRA and must be controlled if discarded. Because these chemicals are desired products, they are usually not discarded. Some air oxidation processes are classified as specific sources of hazardous waste. These sources are included in the hazardous waste process listing for organic chemicals.

The management of nonhazardous wastes essentially remains a State and local function implemented under State and regional solid waste plans.

As the cost of handling wastes increases, some firms will reduce their costs by changing their process to eliminate wastes or by recycling or reclaiming the waste. New plant and equipment expenditures for solid waste control were $42-$45 million for the entire chemical industry in both 1978 and 1979.[62] The annual cost imposed by RCRA on 45 organic chemical plants generating hazardous wastes is estimated to be $10.9 million or an average annual cost of $240,000 per plant.[63] These estimates are based on model plants.

TABLE 8-20. AIR OXIDATION CHEMICALS REGULATED BY RCRA

- Acetaldehyde
- Acetone
- Acetonitrile
- Acetophenone
- Acrylic Acid
- Acrylonitrile
- Cyclohexanone
- Ethylene Dichloride
- Ethylene Oxide
- Formaldehyde
- Formic Acid
- Maleic Anhydride
- Methyl Ethyl Ketone
- Phenol
- Phthalic Anhydride

2. Superfund. The Comprehensive Environmental Response, Compensation, and Liability Act, or Superfund, regulates the cleanup of hazardous waste dumpsites and chemical spills. Superfund provides adequate funding, liability, standards, and authority to the government to recover costs from the responsible parties.[64] Any person in charge of a facility is required to report any "release" of a specified quantity of hazardous waste into the environment immediately. The emphasis of the regulation is to report the release of the wastes and to clean them up first and then recover costs. The Act also develops a tax on all hazardous wastes received at a disposal facility in order to develop a post-closure trust fund. The fee to the chemical industry for this trust fund is less than two percent of their profits.[65]

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9. ECONOMIC IMPACT ANALYSIS

9.1 INDUSTRY STRUCTURE

9.1.1 Industry Definition

There are more than 7,000 organic compounds being produced today. EPA has identified a number of the higher volume and/or higher volatility products. For the purpose of conducting an impact analysis of air pollution regulations, these higher volume chemicals represent the synthetic organic chemicals manufacturing industry (SOCMI). The SOCMI chemicals are produced in a number of different ways. Air oxidation (AO), one of the major processes, uses air rather than oxygen or chemical oxidants as a reactant.

Thirty-six chemicals are produced partially or totally by the AO process. These are listed in Table 3-7 with percentages of total production carried out by the AO process. As the table indicates, nearly half of the 36 chemicals are expected to be produced totally by AO processes. The remaining chemicals may be produced by other means, with AO representing from 5 to 98 percent of the expected 1982 production for any particular chemical. A weighted-by-capacity average of the AO chemicals indicates that 65 percent of total production is by the AO process.

Most of the AO chemicals are found under the Department of Commerce's SIC 2869, Industrial Organic Chemicals, NEC. A few, such as benzaldehyde, phenol, and maleic anhydride, are found under SIC 2865, Cylic Crudes and Cyclic Intermediates, Dyes, and Organic Pigments. AO chemicals are an important part of the U.S. industrial sector: the AO chemicals' value of shipments comprises approximately 10 percent of the total synthetic organic chemical value of shipments; total svnthetic organic chemical shipment value represents 25 percent of the total chemical and allied products (SIC 28) value of shipments; and the chemical and allied products industry is among the largest industrial sectors of the U.S. economy.[1]

For purposes of analysis, the AO industry is defined as producers of chemicals for each of which there currently is at least one AO facility in the United States.

Production, capacity, and other relevant statistics are given here as totals for each AO chemical. The key word is "totals," because a portion of a chemical's production may be by some other process. For instance, only one facility, owned by Oxirane, produces styrene by the AO method; the other 11 styrene-producing facilities use a different process. These 11 firms and the Oxirane facility are intertwined economically (especially from a price standpoint), and any regulation placed on Oxirane will affect the others. In addition, in terms of a New Source Performance Standard, any of the 11 facilities can modify and start producing styrene using AO. Finally, severe data limitations exist if such items as production and sales are disaggregated by facility.

9.1.2 Air Oxidation Chemical's Supply and Capacity

Table 9-1 shows the annual nameplate production capacities for each of the chemicals (in gigagrams). Nameplate capacities are not actual production levels; rather, they represent total production capacity. The total annual production capacities of the AO chemicals range from fewer than three gigagrams for p-t-butyl benzoic acid, a specialty chemical, to 6,508 gigagrams for ethylene dichloride. The six AO chemicals with the largest production capacities are ethylene dichloride, formaldehyde, styrene, dimethyl terephthalate-terephthalic acid, ethylene oxide, and 1,3-butadiene.

Table 9-1 also gives production and capacity utilization figures for the AO chemicals. Capacity utilization, derived by dividing production by capacity, indicates the market conditions confronting producers. A facility is said to be operating at optimal capacity when capacity utilization, in the long run, is 85 percent of nameplate. A low capacity utilization rate usually implies that price increases will be harder to achieve, cost increases will be harder to cover, and new facilities will be harder to justify. Beyond this level, a strain is put on plant equipment. The average capacity utilization rate for the AO chemicals is approximately 78 percent (AO production divided by total AO capacity).

Ethylene dichloride has the greatest production volume of the 36 AO chemicals. Dimethyl terephthalate-terephthalic acid has the largest value

TABLE 9-1. NUMBER OF FACILITIES, CAPACITY, PRODUCTION, CAPACITY UTILIZATION, AND VALUE OF PRODUCTION

36 AO Chemicals
United States
1978

Chemical	No. of facilities[a]	Capacity[a] (Gg)	Production[b] (Gg)	Capacity utilization[c] (%)	Value of production[d] (million $)
Acetaldehyde	5	668	591	88.0	234.6
Acetic acid	10	1389	1266	91.2	421.6
Acetone	20	1284	961	74.9	345.0
Acetonitrile	2	26	NA	--	18.4**
Acetophenone	4	NA	NA	--	--
Acrolein	2	49	NA	--	26.7**
Acrylic acid	3	179	129*	71.9	91.1
Acrylonitrile	6	975	796	81.7	403.6
Anthraquinone	1	2[f]	NA	--	--
Benzaldehyde	5	6	NA	--	7.1**
Benzoic acid	5	143	89	62.4	47.1
1,3-Butadiene	19	1916	1636	85.4	703.5
p-t-Butyl benzoic acid	1	3	NA	--	3.3**
n-Butyric acid	3	6[g]	NA	--	--
Crotonic acid	1	6	NA	--	7.9**
Cumene hydroperoxide	5	4	NA	--	1.9**
Cyclohexanol/ cyclohexanone	8	1141[h]	NA	--	647.6**
Dimethyl terephthalate-terephthalic acid	6	3386[e]	2682[e]	79.2	1307.5
Ethylene dichloride	17	6508	4994	76.7	903.9

TABLE 9-1 (Continued). NUMBER OF FACILITIES, CAPACITY, PRODUCTION, CAPACITY UTILIZATION, AND VALUE OF PRODUCTION

36 AO Chemicals
United States
1978

Chemical	No. of facilities[a]	Capacity[a] (Gg)	Production[b] (Gg)	Capacity Utilization[c] (%)	Value of production[d] (million $)
Ethylene oxide	16	2705	2199	81.3	1081.9
Formaldehyde	53	4050	2924	72.2	327.5
Formic acid	3	37	27	73.2	11.0
Glyoxal	2	NA	NA	--	--
Hydrogen cyanide	12	396	205	51.6	134.3
Isobutyric acid	1	5[g]	NA	--	--
Isophthalic acid	1	109[g]	59	54.3	34.6
Maleic anhydride	10	234	151	64.5	77.9
Methyl ethyl ketone	7	386	272	70.4	114.0
a-Methyl styrene	5	29	25*	85.9	9.9
Phenol	13	1570	1239	78.9	456.0
Phthalic anhydride	11	605	451	74.7	244.4
Propionic acid	4	110	40	36.2	15.0
Propylene oxide	7	1377	929	67.5	442.2
Styrene	12	3831	3136	81.2	1245.0
TOTALS		33,122	24,801	77.8	9364.5

NA = Information not available.

[a] SRI International. 1978 Directory of Chemical Producers, United States of America. Menlo Park, California, 1979.

[b] U.S. International Trade Commission. Synthetic Organic Chemicals, United States Production and Sales, 1978. USITC Publication 10001. Those production numbers denoted with an asterisk (*) are 1977 production figures.

[c] Production as a percentage of capacity.

TABLE 9-1 (Continued). NUMBER OF FACILITIES, CAPACITY, PRODUCTION, CAPACITY UTILIZATION, AND VALUE OF PRODUCTION

36 AO Chemicals
United States
1978

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[d] End 1978 market prices multiplied by production to give value of production. Those chemicals denoted with a double asterisk (**) are estimated based on an average 78 percent capacity utilization rate.

[e] The figures for dimethyl terephthalate (DMT)-terephthalic acid (TPA) include both the acid itself and the dimethyl ester without double counting. In other words, at some plants, process units can interchange TPA and DMT production given the unit's capacity. Individual capacities for DMT and TPA are presented in data sources such that by combining these capacities there exists an overstatement of true capacity for DMT-TPA. The interchangeable process units are identified and the double counting eliminated. The same situation exists for production so the TPA production figure is multiplied by the factor 1.17 (the molecular weight of DMT divided by the molecular weight of TPA) to convert it to equivalent DMT.

[f] Letter from W.P. Bobsein, Toms River Chemical Corp., to L.B. Evans, EPA, February 11, 1980.

[g] Estimated based on data given in letter and attachment from J.C. Edwards, Eastman Kodak Co., to L.B. Evans, EPA, February 6, 1980.

[h] Production capacity of cyclohexanol and cyclohexanone have been reported together.

of production at $1307.5 million. Formaldehyde, with the fourth largest production volume, is well down on the value of production list because of its low selling price.

The value of production, because it takes into account captive consumption, is a much more useful figure than value of sales when looking at the relative "importance" of a chemical. Table 9-2 shows the percentage of each AO chemical's production that is sold. Production consumed captively is used as an intermediate feedstock for downstream processing of other end products within the same plant. Also, the value of production is not the same as value added. Some AO chemicals use other chemicals as raw materials in the production process and simply make the raw material more valuable (useful). Again, however, the value of production is listed because it reflects the relative importance of individual chemicals.

There are about 165 facilities producing AO chemicals in the United States and Puerto Rico today. About 110 (65 percent) of these facilities use some type of AO process; the remainder use other processes to produce the AO chemicals. Some plants produce more than one AO chemical.

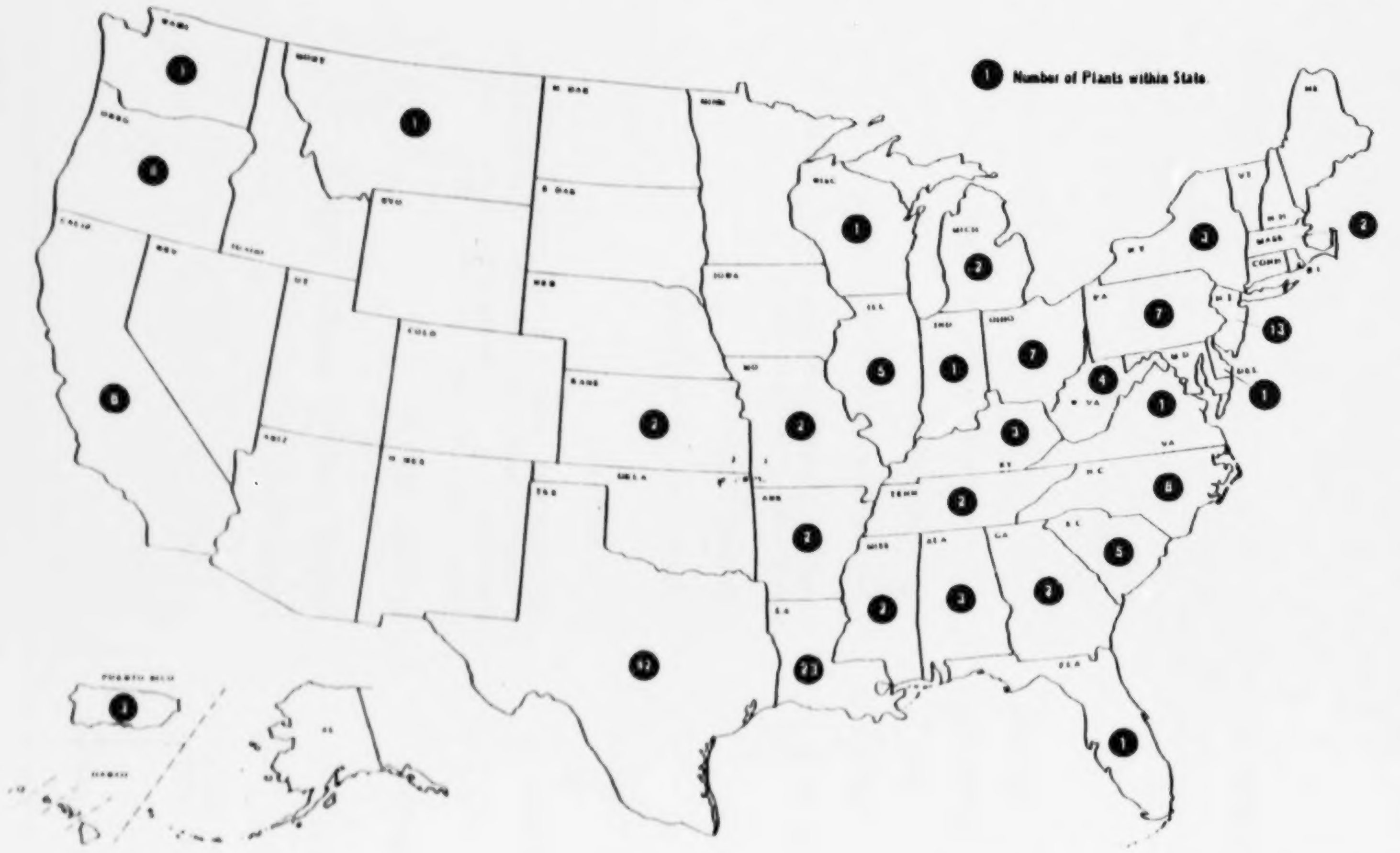
Facilities are located in 30 states and Puerto Rico (see Figure 9-1), and are concentrated along the Gulf Coast (Texas and Louisiana) and the East Coast (New Jersey, Pennsylvania, and North Carolina). More than half of the facilities are located in these five states.

The coastal concentrations reflect facility locations near refineries that site at domestic oil sources or at points of entry for imported oil. Facilities in the central United States are likely to site along natural gas pipeline routes and water transportation arteries. Facility locations in the west may correspond to oil and gas fields.

9.1.3 Industrial Producers

There are 74 companies that produce one or more of the 36 synthetic organic AO chemicals. Table 9-3 lists the companies and the AO chemicals they produce. Of the 74 companies, 50 produce one or two AO chemicals, 17 produce from three to nine chemicals, and seven produce 10 or more. Union Carbide Corporation produces the largest number, 18.

A major share of the organic chemicals partially or fully produced by AO processes is generated by large multi-line chemical companies, subsidiaries of major oil companies, and multi-industry companies with chemical process operations.



1 Number of Plants within State
WASH
1
OREG
8
CALIF
8
NEV
IDAHO
MONT
1
WYO
UT
COLO
ARIZ
N MEX
N DAK
S DAK
NEB
KANS
2
OKLA
TEX
42
MINN
IOWA
MO
2
ARK
2
LA
23
WISC
1
ILL
5
MICH
2
IND
1
OHIO
7
KY
3
TENN
2
MISS
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ALA
3
GA
2
FLA
1
S C
5
N C
8
VA
1
W VA
4
MD
DEL
1
PA
7
N J
13
N Y
3
CONN
R I
MASS
2
VT
N H
ME
AK
HAWAII
PUERTO RICO
3

FIGURE 9-1. AO CHEMICAL PLANT LOCATIONS BY STATE
165 PLANTS
UNITED STATES
1978

TABLE 9-3. INDIVIDUAL COMPANIES AND THE AO CHEMICALS THEY PRODUCE
36 AO Chemicals
United States
1978

Company	Chemicals
Allied Chemical Co.	Acetone, acetophenone, cumene hydroperoxide, cyclohexanol, cyclohexanone, ethylene dichloride, formaldehyde, a-methyl styrene, phenol, phthalic anhydride
American Cyanamid Co.	Acetone, acrylonitrile, glyoxal, hydrogen cyanide
American Hoechst Corp.	Dimethyl terephthalate, styrene
Ashland Oil, Inc.	Maleic anhydride
Atlantic Richfield Co.	1,3-Butadiene, methyl ethyl ketone, styrene
BASF Wyandotte Corp.	Ethylene glycol, ethylene oxide, phthalic anhydride, propylene oxide
B.F. Goodrich	Ethylene dichloride
Borden, Inc.	Acetic acid, formaldehyde
Calcasieu Chemical Corp.	Ethylene oxide
Celanese Corp.	Acetaldehyde, acetic acid, acrylic acid, n-butyric acid, cyclohexanol, cyclohexanone, ethylene oxide, formaldehyde, formic acid, methyl ethyl ketone, propionic acid
Ciba-Geigy Corp.	Hydrogen cyanide
Clark Oil & Refining Corp.	Acetone, a-methyl styrene, phenol
Continental Oil Co.	Ethylene dichloride
Copolymer Rubber and Chemical Corp.	1,3-Butadiene
Cos-Mar, Inc.	Styrene
Crompton & Knowles Corp.	Benzaldehyde

TABLE 9-3 (Continued). INDIVIDUAL COMPANIES AND THE AO CHEMICALS THEY PRODUCE
36 AO Chemicals
United States
1978

Company	Chemicals
Dart Indust., Inc.	Methyl ethyl ketone
Denka Chemical Co.	Maleic anhydride
Diamond Shamrock	Ethylene dichloride
Dow Badische Co.	Acrylic acid, cyclohexanol, cyclohexanone
Dow Chemical, USA	Acetone, ethylene dichloride, ethylene oxide, hydrogen cyanide, phenol, propylene oxide, styrene
DuPont	Acetonitrile, acrylonitrile, cyclohexanol, cyclohexanone, dimethyl terephthalate, formaldehyde, hydrogen cyanide
Eastman Kodak Co.	Acetaldehyde, acetic acid, acetone, n-butyric acid, crotonic acid, dimethyl terephthalate, ethylene oxide, isobutyric acid, propionic acid
El Paso Natural Gas	1,3-Butadiene, styrene
Ethyl Corp.	Ethylene dichloride
Exxon Corp.	Acetone, 1,3-butadiene, methyl ethyl ketone, phthalic anhydride
Firestone Tire & Rubber Co.	1,3-Butadiene
FMC Corp.	Acetic acid
GAF Corp.	Formaldehyde
Georgia-Pacific Corp.	Acetone, formaldehyde, a-methyl styrene, phenol
Getty Oil Co.	Acetone, acetophenone, formaldehyde, a-methyl styrene, phenol
Goodyear Tire & Rubber Co.	Acetone

TABLE 9-3 (Continued). INDIVIDUAL COMPANIES AND THE AO CHEMICALS THEY PRODUCE
36 AO Chemicals
United States
1978

Company	Chemicals
Gulf Oil Corp.	Formaldehyde, styrene
Hercofina	Dimethyl terephthalate, terephthalic acid
Hercules, Inc.	Cumene hydroperoxide, formaldehyde, hydrogen cyanide
Inter'l Minerals & Chemical Corp.	Cumene hydroperoxide, formaldehyde, hydrogen cyanide
Kalama Chemical, Inc.	Benzaldehyde, benzoic acid, phenol
Koppers Co., Inc.	Maleic anhydride, phthalic anhydride
Mobil Corp.	1,3-Butadiene
Monroe Chemical, Inc.	Benzaldehyde
Monsanto Co.	Acetic acid, acetone, acrylonitrile, 1,3-butadiene, cyclohexanol, cyclohexanone, formaldehyde, hydrogen cyanide, maleic anhydride, phenol, phthalic anhydride, styrene
Neches Butane Products Co.	1,3-Butadiene
Nipro, Inc.	Cyclohexanol, cyclohexanone
Northern Natural Gas Co.	Ethylene oxide
Northwest Indust., Inc.	Benzoic acid
Occidental Petroleum, Inc.	Formaldehyde, phthalic anhydride
Olin Corp.	Ethylene oxide, propylene oxide
Oxirane Corp.	Acetone, propylene oxide, styrene
Pennwalt Corp.	Cumene hydroperoxide
Pfizer, Inc.	Benzoic acid

TABLE 9-3 (Continued). INDIVIDUAL COMPANIES AND THE AO CHEMICALS THEY PRODUCE
36 AO Chemicals
United States
1978

Company	Chemicals
Phillips Petroleum Co.	1,3-Butadiene
PPG Indust., Inc.	Ethylene dichloride, ethylene oxide
Publicker Indust., Inc.	Acetaldehyde, acetic acid
Puerto Rico Olefins Co.	1,3-Butadiene
Reichold Chems., Inc.	Cumene hydroperoxide, formaldehyde, maleic anhydride, phenol
Rockland Indust., Inc.	Formic acid
Rohm and Haas Co.	Hydrogen cyanide
Shell Chemical Co.	Acetaldehyde, acetone, acrolein, 1,3-butadiene, p-t-butyl benzoic acid, ethylene dichloride, ethylene oxide, methyl ethyl ketone, phenol
Standard Oil Co. (CA)	Acetone, phenol, phthalic anhydride
Standard Oil Co. (IN)	1,3-Butadiene, isophthalic acid, maleic anhydride, styrene, terephthalic acid
Standard Oil Co. (OH)	Acetonitrile, acrylonitrile, hydrogen cyanide
Stauffer Chemical Co.	Ethylene dichloride
Stephan Chemical	Phthalic anhydride
Sun Co., Inc.	Styrene
Sunolin Chemical Co.	Ethylene oxide
Tenneco, Inc.	Benzaldehyde, benzoic acid, 1,3-butadiene, maleic anhydride
Texaco, Inc.	Ethylene oxide, propylene oxide

TABLE 9-3 (Continued). INDIVIDUAL COMPANIES AND THE AO CHEMICALS THEY PRODUCE
36 AO Chemicals
United States
1978

Company	Chemicals
Toms River Chemical Corp.	Anthraquinone
UOP, Inc.	Acetophenone, benzaldehyde
Union Carbide Corp.	Acetic acid, acetone, acetophenone, acrolein, acrylic acid, 1.3-butadiene, n-butyric acid, cyclohexanol, cyclohexanone, ethylene dichloride, ethylene oxide, formic acid, glyoxal, methyl ethyl ketone, phenol, propionic acid
Univar Corp.	Formaldehyde
US Steel Corp.	Acetone, cumene hydroperoxide, maleic anhydride, a-methyl styrene, phenol, phthalic anhydride, styrene
Vulcan Materials Co.	Ethylene dichloride
Wright Chemical Corp.	Formaldehyde

SOURCE: SRI International. 1978 Directory of Chemical Producers, United States of America. Menlo Park, California, 1979.

Table 9-4 gives the single, largest producer for each AO chemical and the percentage of the AO chemical's total capacity owned by that company. In general, the higher the production volume of the AO chemical, the lower the percentage of total capacity any one company will own. Those AO chemicals that are produced by only one company typically are produced in small volumes. The issue of market concentration is discussed further in Section 9.1.12.

9.1.4 Employment

Employment in 1978 under SIC 286 (Industrial Organic Chemicals) was 139,000.[2] The production value of SOCMI AO chemicals is approximately 10 percent of the SIC 286 value of production. Thus, about 13,900 employees (10 percent of 139,000) were employed producing chemicals on the AO list.

9.1.5 Industry Finances

Although it has recently passed through a period of declining profit margins, the chemicals industry is large, with considerable resources available for capital investment.

For the chemicals industry as a whole (including AO process chemical manufacturers, non-AO process chemical manufacturers, and a certain amount of non-chemical business), the profit margin (after-tax earnings as percentage of net sales) increased from 1971 through the third quarter of 1974 and then plummeted in the fourth quarter of 1974 and throughout 1975 and 1976. The years 1977 and 1978 saw slight increases in the profit margin.[3] Despite greater increases in chemical profit margins more recently,[4] the last four or five years have not brought heavy cash inflows from profits (see Figure 9-2).

The major reasons for low profitability include the recession (reduced demand for construction, automobiles, and durable goods reduces demand for chemicals used in their manufacture), continuing increases in the prices of energy and feedstocks, and generally low capacity utilization. When chemical plants cannot operate at full capacity, high fixed costs must be spread over lower volumes. While unit costs increase, reduced demand inhibits price increases. Profit margins, thus, are squeezed and volumes stagnate or fall, lowering total profits. Capacity utilization rates exceeded 80 percent in the years 1971 through 1974. During the next four years (1975 through 1978), capacity utilization rates dropped below 80 percent. The

TABLE 9-4. THE LARGEST PRODUCER OF EACH AO CHEMICAL AND THE PERCENTAGE OF THE AO CHEMICAL'S TOTAL CAPACITY THE LARGEST PRODUCER OWNS

36 AO Chemicals
United States
1978

Chemical	Single largest producer	Percentage of total capacity
Acetaldehyde	Celanese	61
Acetic acid	Celanese	41
Acetone	Shell Chemical	23
Acetonitrile	NA	NA
Acetophenone	NA	NA
Acrolein	NA	NA
Acrylic acid	Celanese	54
Acrylonitrile	Monsanto	40
Anthraquinone	Toms River Chemical	100
Benzaldehyde	NA	NA
Benzoic acid	Kalama Chemical	49
1,3-Butadiene	Naches Butane Products	17
p-t-Butyl benzoic acid	Shell Chemical	100
n-Butyric acid	NA	NA
Crotonic acid	Eastman Kodak	100
Cumene hydroperoxide	NA	NA
Cyclohexenol/ cyclohexanone	DuPont	29
Dimethyl terephthalate	DuPont	42
Ethylene dichloride	Dow Chemical	33
Ethylene oxide	Union Carbide	42
Formaldehyde	Celanese	19

TABLE 9-4 (Continued). THE LARGEST PRODUCER OF EACH AO CHEMICAL AND THE PERCENTAGE OF THE AO CHEMICAL'S TOTAL CAPACITY THE LARGEST PRODUCER OWNS
36 AO Chemicals
United States
1978

Chemical	Single largest producer	Percentage of total capacity
Formic acid	Union Carbide	61
Glyoxal	NA	NA
Hydrogen cyanide	DuPont Rohm and Haas	33 33
Isobutyric acid	Eastman Kodak	100
Isophthalic acid	Standard Oil (IN)	100
Maleic anhydride	Monsanto	20
Methyl ethyl ketone	Shell Chemical	39
a-Methyl styrene	Allied Chemical	45
Phenol	Allied Chemical	17
Phthalic anhydride	Koppers	25
Propionic acid	Union Carbide	62
Propylene oxide	Oxirane	44
Styrene	Dow Chemical Monsanto	18 18
Terephthalic acid	Standard Oil (IN)	88

NA = Information on individual company capacities not available.

SOURCE: SRI International. 1978 Directory of Chemical Producers, United States of America. Menlo Park, California, 1979.

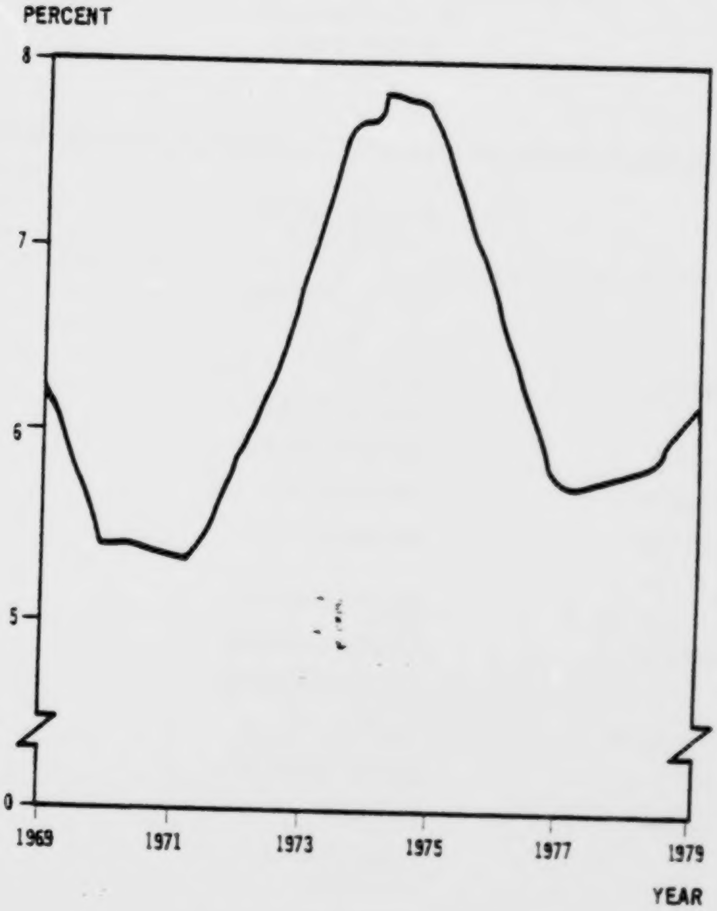

FIGURE 9-2. AFTER-TAX EARNINGS AS A PERCENTAGE OF NET SALES
(Annual Profit Margins)
CHEMICALS AND ALLIED PRODUCTS (SIC 28)
UNITED STATES
1969-1979

SOURCE: "Earnings Gain Off, But Better Than Expected." Chemical and Engineering News, p.9, February 18, 1980.

fluctuation in capacity utilization correlates closely with the increasing profit margins in the earlier years and decreasing profit margins in the later years.

Profits are only part of the picture, however. Internal cash flow comes not only from after-tax profits but also from depreciation charged to past investments. With a large capital stock already in place, the chemicals industry has a substantial cash flow from depreciation alone. The cash flow, however, is limited in comparison to inflated capital requirements for replacement plants and, in many cases, requirements for plants of much larger scale needed to adopt the latest efficient technology.

Chemical and Engineering News examined a sample of 20 chemical companies (19 of which produce AO chemicals) and found that the standard current ratio (current assets divided by current liabilities) dropped to 2.1 at year-end 1978 from 2.3 the previous year. The ratio was 2.1 in 1974, but was 2.4 in 1975. At the same time, the cash ratio (coverage of current liabilities with cash and marketable securities) had deteriorated. It stood at 0.23 in 1978, compared to a high of 0.33 in 1975 and 0.28 in 1974. Thus, the short-term liquidity of chemical firms has been squeezed recently.[5]

However, the ability of the industry to raise capital for long-term investment is based in large measure on the yields the industry offers investors. Returns on common stock have been strong over the last decade as a whole and, despite some recent difficulties, are still approximately equal to those of other industries. These facts, as shown below, indicate that the chemicals industry continues to offer competitive yields and will remain competitive in its ability to attract investment capital.

From 1970 to 1980, the chemicals segment of the Fortune 500 company listing showed an annual return to investors of 11.97 percent. This was higher than the 9.44 percent return for all industries. Total return to investors includes the sum of stock price appreciation and dividend yield. Performance has dropped in recent years but continues to at least approximate the average among industries. Return on stockholders' equity for the chemicals segment of the Fortune 500 was 15.2 percent and 13.9 percent, respectively, in 1979 and 1980. This is slightly below the median rates for all industries, which were 15.9 percent and 14.4 percent in the same years.

Results for the Fortune Second 500, i.e., the next size tier of companies, showed roughly the same pattern. Chemical companies offered better than average total return to stockholders over the last decade and approximately average returns on equity in the last two years.

These facts imply that the chemicals industry remains competitive in its attractiveness to investors and that the industry should be able to attract large sums, given its large size, to finance future investments. Cash flow from depreciation allowances on existing assets also will contribute substantially to funds available for investment.

The debt ratio (long-term debt as a percentage of long-term debt plus equity) increased slightly, from 27.8 percent in 1977 to 27.9 percent in 1978, but did not increase much more than the ratio for all manufacturing, which stood at 24.4 percent in 1978, down from 24.6 percent in 1977.[6]

Aggregate industry cash flow from various sources is presented in Table 9-5, which indicates that, despite problems in profitability, the industry's cash flow has grown continually. Capital expenditures, a major use of cash flow, were $5.1 billion in 1978, down slightly from $5.5 billion in 1977.[7]

In summary, the chemicals industry has gone through a period (1974-1978) of slow profit growth, but it remains a large generator of cash flow for new investments. More important to the investment behavior of the chemicals industry is that 1979 has shown much stronger profits and, barring a deep recession, demand should be strong enough to support increased capacity utilization and higher profit margins. The industry as a whole will be able to raise necessary cash if it foresees such opportunity for profitable returns on its investments.

9.1.6 End Uses

This section presents brief surveys of the major AO chemical-using industries. The surveys include both AO chemicals and non-AO chemicals to provide a background on the context in which AO chemicals are used.

AO chemicals have many uses. They are used as plastics, textile fibers, rubber, surface coatings, dyes, food additives, fragrances, adhesives, drugs, and other substances.

There are two important characteristics of the AO chemicals industry in general. First, many AO chemicals serve as intermediate chemicals in

TABLE 9-5. AGGREGATE CASH FLOW STATISTICS (NOMINAL $), CHEMICALS AND ALLIED PRODUCTS (SIC 28)
United States
1974-1978

Item	1978 Million $	1978 % of total	1977 Million $	1977 % of total	1976 Million $	1976 % of total	1975 Million $	1975 % of total	1974 Million $	1974 % of total
Net income	3085.4	33.6	2754.0	30.6	2855.3	32.9	2427.1	29.1	2829.1	40.0
Depreciation and depletion	3197.0	34.8	2812.7	31.5	2420.1	27.9	2155.2	26.6	1963.8	27.8
Deferred taxes	353.4	3.8	356.6	4.0	373.9	4.3	416.6	5.1	307.0	4.3
Other internal sources	929.6	10.1	1214.4	13.5	666.4	7.7	591.0	7.3	489.7	6.9
Long-term debt	1544.5	16.8	1609.1	17.9	2219.5	25.6	2333.3	28.8	1386.6	19.6
Stock	83.8	0.9	229.9	2.5	142.9	1.6	187.7	2.3	99.4	1.4
Total	9193.7	100.0	8996.7	100.0	8678.1	100.0	8110.9	100.0	7075.6	100.0
Dividends	1317.1	14.3	1183.5	13.1	1054.9	12.1	924.1	11.4	898.4	12.7
Capital expenditures	5080.4	55.3	5488.0	61.0	5701.6	65.7	5191.8	64.0	4455.3	63.0
Additions to working capital	863.1	9.4	520.2	5.8	545.3	6.3	714.3	8.8	615.0	6.7
Reduction of long-term debt	878.7	9.5	746.5	8.3	728.3	8.4	742.7	9.2	380.1	5.4
Other applications	1054.4	11.5	1058.5	11.8	648.0	7.5	538.0	6.6	726.8	10.3
TOTAL	9193.7	100.0	8996.7	100.0	8678.1	100.0	8110.9	100.0	7075.6	100.0

SOURCE: Facts and Figures for the U.S. Chemical Industry. Chemical and Engineering News. P. 49. June 11, 1979. Data are for 15 major chemical firms: Allied Chemical, American Cyanamid, Celanese, Diamond Shamrock, Dow Chemical, DuPont, Ethyl Corp., Hercules, Monsanto, Olin, Pennwalt, Rohm & Haas, Stauffer Chemical, Union Carbide, and Williams Co.

the production of several other chemicals which, in turn, have numerous end uses and final products. A single organic chemical, thus, can be traced along many branches that lead to other chemicals and various end uses.

Second, while the uses of AO chemicals are many, the major end uses are not. Plastics and textile fibers account for the bulk of consumption of the AO chemicals studied here.

The concentration of AO chemical consumption in relatively few industries -- plastics and fibers -- is shown in Table 9-6. Ten chemicals account for 80 percent of total estimated dollar sales of all AO chemicals studied. (It should be noted, however, that some of the chemicals are produced partially by non-AO processes; see Table 3-7.) Nine of the 10 top chemicals are used largely for the manufacture of plastics or textile fibers. The other, 1,3-butadiene, is used mainly to make synthetic rubber for automobile tires.

Demand for plastics and fibers is strong because of their structural, non-structural, and substitutional uses. Although AO chemicals have many specialty uses, the plastics and fibers markets create considerable demand for AO chemicals. In a sense, the plastics and fibers uses help to distinguish the AO chemicals from myriad other organic chemicals that serve smaller, less well-known markets.

At the same time, other uses of AO chemicals can be important. Pharmaceuticals, for example, account for just 6 percent of acetone volume but are important chemical products. Small uses also may signify potentially large uses that have not been developed fully yet. Nonetheless, for this analysis, the basic characterization of the AO chemicals as primarily intermediates for the plastics and textile fibers industries is a useful way to describe the list succinctly.

9.1.6.1 The Plastics Industry. As already noted, the major use of AO chemicals is in the plastics sector of the chemicals industry. In 1977, shipments of plastics and resins totaled $11.6 billion. Total plastics sales equalled 14 percent of all chemicals industry sales.[8]

Plastics are long-chained molecular substances. In this section, the term "plastic" is used interchangeably with the term "resin." Technically, not all resins are plastics. Some resins are used as adhesives, for example, in plywood. Plastics are fairly tough resins that usually can be made into

TABLE 9-6. AO CHEMICALS BY VALUE OF PRODUCTION WITH EACH CHEMICAL'S MAJOR END USE PRODUCTS

14 AO Chemicals
United States
1978

Top 14 AO chemicals ranked by production value ($)	Value (million $)	Cumulative percentage of total AO value[a]	Major end use products
1. Dimethyl terephthalate-terephthalic acid	1307.5	14	Polyester fibers, films
2. Styrene	1245.0	27	Plastics, rubber
3. Ethylene oxide	1081.9	39	Anti-freeze, polyester
4. Ethylene dichloride	903.9	48	Polymers, resins
5. 1,3-Butadiene	703.5	56	Rubber
6. Cyclohexanol/cyclohexanone	647.6	63	Nylon
7. Phenol	456.0	68	Plastics, adhesives
8. Propylene oxide	442.2	72	Urethane plastic, polyester
9. Acetic acid	421.6	77	Vinyl, cellulose acetates
10. Acrylonitrile	403.6	81	Acrylic fibers, ABS and SAN plastics
11. Acetone	345.0	85	Cellulose acetate fibers, plastics
12. Formaldehyde	327.5	88	Plasticizers, plastics, polyester
13. Phthalic anhydride	244.4	91	Plastics
14. Acetaldehyde	234.6	94	Intermediate for numerous chemicals
Total Production Value[a] (36 AO Chemicals)	9364.5		

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[a] Excludes data for 5 AO chemicals under study. Those exluded are small volume chemicals, however, so the percentages would not change much. Sales volumes are estimates using 1978 production volumes and 1978 market prices (Table 9-13).

structural shapes.[9] Nonetheless, the term "plastics" is used most frequently because it is easier to conceptualize in discussing end uses.

In terms of production volume, the largest plastic is polyethylene. In 1978, 5,100 gigagrams of polyethylene were produced in the United States. Polyvinylchloride is second, with production of 3,100 gigagrams. Polystyrene is third, with 2,000 gigagrams produced. Polypropylene is fourth, with 1,300 gigagrams produced. Phenolics are fifth, with 900 gigagrams produced. Other kinds of plastics also have substantial production volumes. Production of all kinds of plastics totaled 17,100 gigagrams in 1978.[10] Within broad classes of plastics, it may be noted, there are many varieties that differ only slightly in molecular composition but that have different end-use properties.

The plastics industry has grown rapidly and has penetrated many end-use markets. The fact that AO chemicals are used in the manufacture of plastics means that AO chemicals are used extensively throughout the economy. Even the service sectors, which use relatively few materials, rely upon some amount of plastics indirectly in their equipment and accessories.

Plastics have various properties that make them suitable for different end uses. Each plastic is unique in terms of its combination of functional properties -- flexibility, solubility, resistance to heat and sun, behavior under stress, clarity, and so on. Plastics also differ in price: styrene, for example, is inexpensive, while fluorocarbon plastics are very expensive. Finally, plastics differ in terms of processability -- moldability, extrudability, and so on. Consequently, each kind of plastic is used in certain end uses, although in many end uses there is competition among plastics and between plastics and other materials. Table 9-7 shows a breakdown of the major plastics and ultimate end-use markets.

9.1.6.2 The Textile Fibers Industry. The textile fibers industry is related to the plastics industry in that many plastics and fibers share common resins. A fiber is similar to its related plastic except that the molecules in a fiber may be longer and are aligned in the production process so that the filament structure has considerable strength.

There are three major classes of fibers -- natural, inorganic, and synthetic organic. Natural fibers are made from plant or animal sources directly, without chemical conversion. These include cotton, wool, and

TABLE 9-7. CONSUMPTION OF PLASTIC MATERIALS AND SYNTHETIC RESINS BY END USE SECTORS
United States
1976

Product	Consumption (gigagrams)											
	Pack-aging	Con-struction	House-wares	Electric and electronic	Trans-portation	Paints	Toys	Furni-ture	Appli-ances	Other domestic	Exports	Total
Polyethylene												
Low-density	1143	91	532	155	0	0	50	11	5	352	234	2573
High-density	600	127	159	0	9	0	68	0	0	295	157	1416
	1743	218	691	155	9	0	118	11	5	647	391	3989
Polyvinylchloride	272	1000	45	159	130	54	34	102	20	471	236	2525
Polystyrene												
Solid	398	50	175	100	0	0	155	45	70	34	82	1109
Foam	127	0	55	0	0	0	0	0	0	66	0	248
ABS and SAN	16	114	9	32	77	0	41	5	59	161	20	534
Other	0	0	0	0	0	11	0	0	0	243	9	264
	541	164	239	132	77	11	196	50	129	504	111	2155
Polypropylene	195	7	59	39	166	0	32	14	41	430	177	1159
Polyurethane foam	20	120	0	0	220	0	0	232	36	109	9	748
Phenolic	5	277	23	91	23	11	0	27	39	86	11	593
Polyester	0	84	0	25	73	5	0	9	16	193	39	443
Amino	7	320	16	16	0	34	0	7	0	145	14	559
Alkyd	0	0	0	0	0	295	0	0	0	18	7	320
Acrylic	0	61	0	0	34	45	0	0	2	239	23	405
Cellophane	91	0	0	0	0	0	0	0	0	5	52	148
Courmaroneindene	18	14	0	0	0	16	0	0	0	89	0	136
Epoxies	0	7	0	7	7	41	0	0	2	32	23	118
Cellulosics	20	2	0	2	7	0	2	0	0	36	34	105
Polyamides	0	0	0	11	20	0	0	0	5	20	14	66
Other	75	18	5	32	32	0	2	0	23	23	43	252
TOTAL	2989	2291	1077	668	798	514	384	452	318	3048	1184	13720

flax. Inorganic fibers are filament-shaped inorganic substances. Examples are steel wool and asbestos insulation material.

Synthetic organic fibers are derived from organic materials and are produced through either regeneration or substantial chemical conversion. One major class of synthetics is the cellulosic class, which includes rayon and acetates. Cellulosics are said to be semi-synthetics because their process uses regenerated cellulose obtained from high-purity wood pulp or cotton. Pure synthetics are the other major class of synthetics. Examples of these are polyester, nylon, and acrylics. These are manufactured via chemical processes that involve substantial chemical conversion to produce the final molecules. All synthetic organic fibers, like natural fibers, contain carbon. Carbon atoms provide the basis for the linkages that allow long polymer molecules to form.

The largest volume synthetic fiber is polyester. Polyester accounts for 45 percent of all synthetic fibers. Nylon is second, with 28 percent. Acrylics, polyolefins, and rayon each account for about 8 percent of the synthetics total.[11] Table 9-8 illustrates the end-uses of synthetic fibers as a group.

9.1.6.3 Other Industries. As noted earlier, AO chemicals are used in other industries, including the rubber, surface coating, adhesive, food additive, dye, fragrance, solvent, and drug industries.

The rubber industry, which includes both natural and synthetic rubber, is fairly large. Of synthetic rubber (or elastomers, as the term is used generically), styrene-butadiene rubber (SBR) is the largest industry, accounting for 50 percent of the 3,000 gigagrams of synthetic elastomers produced in 1978.[12] Table 9-9 shows the consumption of synthetic elastomers by end use.

The surface coating industries include paints, lacquers, finishes, and sealants. The main use of AO chemical derivatives is in the base vehicle to hold pigments in paints. AO chemicals are useful as vehicles because they form large polymer sheets over the surfaces of other substances.

Adhesives are another use for AO chemicals. As noted earlier, resins are used as bonding agents in many applications. In 1972, synthetic resins accounted for 69 percent of the $833 million in adhesives shipments; natural base adhesives accounted for 14 percent.[13]

TABLE 9-8. CONSUMPTION OF MAN-MADE FIBERS BY END USE, AND AS A PERCENTAGE OF ALL FIBERS CONSUMPTION BY END USE
United States
1970 and 1975

End Use	Consumption (gigagrams) 1970	1975	Percentage of all fibers 1975
Home Furnishings			
Carpets and rugs	499	723	98.1
Draperies and upholstery	145	144	57.8
Sheets	50	89	41.7
Blankets	41	47	88.0
Curtains	11	20	75.9
Bedspreads and quilts	12	15	31.4
Towels	1	6	5.1
Other	505	735	96.6
Subtotal	1,264	1,780	80.2
Apparel			
Men's suits, slacks, and coats	136	231	59.5
Women's dresses	185	184	80.5
Women's suits, slacks, and coats	105	175	64.7
Shirts	88	113	57.8
Women's blouses	41	100	75.9
Women's under- and nightwear	81	70	73.2
Apparel linings	83	52	60.2
Uniforms and work clothes	37	50	46.0
Anklets and socks	30	39	71.7
Sweaters	35	35	77.2
Men's under- and nightwear	15	28	22.0
Robes and loungewear	21	27	73.4
Hosiery	30	24	100.0
Swimwear and other recreational wear	14	14	36.9
Other	80	80	54.0
Subtotal	980	1,223	64.5

TABLE 9-8 (Continued). CONSUMPTION OF MAN-MADE FIBERS BY END USE, AND AS A PERCENTAGE OF ALL FIBERS CONSUMPTION BY END USE
United States
1970 and 1975

End Use	Consumption (gigagrams) 1970	1975	Percentage of all fibers 1975
Industrial and Other Consumer Goods			
Tires	254	232	100.0
Reinforced plastics	111	169	93.7
Retail piece goods	91	186	73.9
Medical, surgical, and sanitary products	38	59	60.8
Rope, cordage, and tape	35	58	78.5
Coated fabrics	9	35	55.4
Sewing thread	11	20	39.1
Other	175	262	67.6
Subtotal	723	1,021	77.0
TOTAL	2,967	4,024	73.3

SOURCE: C.H. Kline & Co. The Kline Guide to the Chemical Industry. Fairfield, New Jersey, C.H. Kline & Co., 1977. Table 3-10, P. 174.

TABLE 9-9. PERCENTAGE OF TOTAL SYNTHETIC RUBBER CONSUMED BY END USE
United States
1976

End use	Percentage of total weight consumed
Tires, tubes and tire products	57.7
Molded goods	
Industrial rubber	11.0
Automotive	4.7
Footwear	3.0
Plastic impact modifiers	1.8
Belting, hoses and gaskets, etc.	1.8
Wire and cable	1.4
Adhesives	1.2
Coatings	1.1
Other	16.3
Total	100.0

SOURCE: C. H. Kline & Co. The Kline Guide to the Chemical Industry. Fairfield, New Jersey, C.H. Kline & Co., 1977. Table 3-17, p. 106.

Many AO chemicals are used in small amounts as food additives. They help to ensure freshness and moisture or to give color and tartness. AO chemicals also are used as flavorings, fragrances, and perfumes. These products, in turn, are used in many consumer goods.

Dyes consume a substantial amount of AO chemicals, particularly anthraquinone. In 1976, 116 million kilograms of dyes were produced.[14]

Substantial amounts of AO chemicals are used as solvents. Methyl ethyl ketone is a good example. Organic solvents are used in a wide number of products, as well as in many industrial processes.

The drug industry uses some AO chemicals. While drugs account for small quantities of AO chemicals, their value in the economy is high. Many other industries use AO chemicals to some degree (see Section 9.1.7), but the industries mentioned in this section are the largest users.

9.1.6.4 Growth in End Use Production. The chemical processing industry (CPI) recently has experienced a slowdown in its production growth rate.[15] Historically, CPI growth usually has exceeded the growth of the overall economy: from 1954 to 1979, the CPI grew at an average annual rate of 7.8 percent compared with a rate of 4.6 percent for all manufacturing. Merrill Lynch, Pierce, Fenner & Smith, Inc. projects that, in 1985, the growth in chemical output will slow to 5.8 percent.[16] This would still be greater than the annual growth rate in GNP, but the gap would be narrowed. Although many sources believe that the growth rate will remain at its slower pace, there are a few optimistic forecasters: Arthur D. Little, Inc. projects growth in petrochemicals will run 7 to 8 percent a year in real dollar terms over the next five years.[17] Recently, growth projections for the chemicals industry have been toned down. The May 12, 1980 issue of Chemical Marketing Reporter projects only a 4 percent growth rate through the 1980's.

The CPI's spectacular growth has been due to substitution of synthetic chemicals for natural products. Elastomers have been substituted for natural rubber, plastics for paper and metals, and synthetic fibers for cotton, wool, and silk. Now this penetration is seen as leveling off.

Charles H. Kline & Co., Inc. has projections to 1983 for specific plastic types[18] and elastomers.[19] The projected growth rates for some end uses mentioned in the preceding section are given below, and they are assumed to apply through 1986.

The markets for low-density polyethylene will start to mature, especially in food packaging. Polyethylene production should grow at an average rate of 6 percent a year through 1983, down from the 1968 to 1978 average rate of 8.1 percent.

High-density polyethylene production will do better, expanding at an average rate of 7 percent through 1983. The market will expand with automobile producers replacing metal with this plastic in fuel tanks to reduce weight in automobiles. Industrial containers, corrugated drain pipes, and consumer packaging all will be expanding markets for high-density polyethylene.

The average annual growth rate for polyvinylchloride (PVC) is predicted to increase over its historical rate of 8 percent to 9 percent through 1983. There will be increased usage of PVC in bottles, as well as in pipe, conduit, and other construction materials.

Polystyrene will show good growth in the disposable and packaging markets. It should increase by an average rate of 6 percent per year. However, a current study underway at EPA states that polystyrene growth probably will show no growth in the next five years.

Phenolics represent a mature market. They will follow the general growth of the U.S. economy and grow approximately 3.5 percent per year.

Polyurethane has had a very successful 11.2 percent per year historical growth rate. From now to 1984, this rate should drop to an average of 8.7 percent per year. This will be caused by the maturing of the furniture and transportation markets which represent 75 percent of polyurethane sales. However, the other quarter of polyurethane demand, rigid foam, should grow at 13 percent per year due to a large increase in the installation of insulation in industrial buildings. Rigid urethane foam is said to have better cost performance than such traditional materials as fiberglass.

Acrylonitrile-butadiene-styrene should increase at an average annual rate of 7 percent, due mostly to the replacement of metal parts in automobiles with these resins.

Reduced land vehicle weight again is the reason for a large demand in certain plastics. Unsaturated polyesters are expected to increase an average of 8.5 percent per year for this reason.

U.S. demand for acrylics is projected to grow at an average of 6 percent per year. The growth in alkyds is projected to be only 2 percent per year through 1983. Consumers will be substituting alkyds for acrylic and epoxy coatings. Cellulosics will grow at an average rate of only 2 percent per year due to competition from other plastics, especially polypropylene in film applications. With increased demand for rust-proof coatings as the driving force, epoxies sales should grow at an average annual rate of 10 percent per year.

C. H. Kline & Co. estimates that the plastics, materials, and resins industry as a whole will experience an average annual growth rate of 7 percent through 1983. If this proves to be true, it will be good news for the many AO chemical producers who supply the materials for producing plastics.

The elastomers market will not fare as well as plastics. C. H. Kline & Co. has projected an average annual growth rate of 3.1 percent through 1983. SBR, which represents half of the elastomers total production, wil increase at a rate of only 1 to 2½ percent a year. This is because SBR is tied so closely to the automotive industry, with 65 percent of SBR used in passenger car tires. With radial tires and smaller automobiles (hence, smaller tires) becoming more popular, the growth prospects for SBR are dim.

The other major end use of AO chemicals, fabrics, should experience moderate growth. With the industry maturing, growth through 1986 is not expected to be much greater than the overall growth in GNP.[20] Nylon will show the strongest growth due to increasing demand, and polyester growth should be steady.

9.1.7 Individual AO Chemicals

The following individual profiles indicate the chemical users as well as the projected average annual growth rates for the larger volume chemicals. Published sources give growth rate projections through 1983, and these are assumed to be true through 1986. Overall growth for AO chemicals, using a weighted-by-capacity average, is projected to be 4.7 percent.

9.1.7.1 Acetaldehyde. Acetaldehyde is used as an intermediate in the production of a number of chemicals. Half of total acetaldehyde consumption is for the production of acetic acid and acetic anhydride which, in turn, are used in large part to make plastics. Other substances derived from acetaldehyde are pentaerythritol, pyridines, peracetic acid, crotonaldehyde, chloral, 1,3-butanediol, glycol, lactic acid, and glyoxal. Acetaldehyde is expected to have an average annual growth rate in production of 4 percent through 1986.[21]

9.1.7.2 Acetic Acid. Acetic acid is used to manufacture a number of plastics and other substances. Forty percent of acetic acid is used in the production of vinyl acetate monomer. Twenty-three percent is used in making cellulose acetate. Acetic esters, such as ethyl acetate and butyl acetate, account for 13 percent. Terephthalic acid and dimethyl terephthalate, which are used to manufacture polyester, account for 10 percent.

Miscellaneous textile industry processes, such as wool dyeing, silk cleaning, printing, finishing, and laundering, use 3 percent of all acetic acid.

Chloroacetic acid, which is used in food, drug, cosmetic, and dentifrice products, synthetic detergents, and oil well drilling mud, accounts for 2 percent. Other substances, including grain fumigants, pharmaceuticals, rubber chemicals, and photographic chemicals, use 9 percent.

Acetic acid is expected to have an average annual growth rate of 4.6 percent through 1986.[22]

9.1.7.3 Acetone. Acetone is used to manufacture several plastics, solvents, and other substances. Methyl methacrylate accounts for 25 percent of all acetone consumption. Methyl isobutyl ketone accounts for 14 percent. Solvents for protective coatings use another 10 percent.

Pharmaceuticals use 6 percent of the acetone total. Use as a chemical processing solvent accounts for another 5 percent of acetone volume. Methacrylic acid and higher methacrylates use 5 percent. Bisphenol A, used in making epoxy resins, consumes another 5 percent.

Additional uses of acetone include cellulose acetate spinning solvent (4 percent), hexylene glycol (3 percent), diacetone alcohol (2 percent), methyl isobutyl carbinol (2 percent), isophorone (2 percent), mesityl oxide (1 percent), and other substances (16 percent).

The projection for acetone is a 4 percent average annual increase in production through 1986.[23]

9.1.7.4 Acetonitrile. Acetonitrile is used as a solvent, as a chemical intermediate for vitamin B, and in pyrimidines and pharmaceutical uses.

This chemical is a byproduct from the production of acrylonitrile; the plants that produce acetonitrile are the same plants that produce acrylonitrile. It is assumed that acetonitrile and acrylonitrile have similar growth projections (4 percent).[24]

9.1.7.5 Acetophenone. Acetophenone is used in the production of solvents, drugs, polymers, and paints.

9.1.7.6 Acrolein. Acrolein is used primarily as an intermediate chemical in the production of glycerin and acrylic acid. It is used also in the manufacture of methionine hydroxy analogue.

9.1.7.7 Acrylic Acid. Acrylic acid is used in the manufacture of acrylates, which are used in emulsion and solution polymers in coatings, finishes, binders, paints, floor polishes, and adhesives. The projected annual average growth rate for acrylic acid is 5 percent.[25]

9.1.7.8 Acrylonitrile. Approximately half (52 percent) of acrylonitrile use is in the production of acrylic and modacrylic fibers. These are used mainly in making sweaters, handcraft yarn, pile, and fleece, as well as carpet static, blankets, draperies, and upholstery.

ABS and SAN plastics account for another 22 percent. ABS plastics are used in pipes, pipe fittings, automobile components, and other uses. SAN plastics are used in drinking tumblers, automotive dashboards, and other items.

Additional uses of acrylonitrile include the production of adiponitrile (11 percent) used in the manufacture of nylon 6,6, nitrile elastomers (4 percent), acrylamide (4 percent) used in secondary and tertiary oil recovery and waste treatment, nitrile barrier resins (1 percent) for packaging, and other substances (5 percent).

Acrylonitrile is projected to have an average annual growth rate of 4 percent through 1986.[26]

9.1.7.9 Anthraquinone. Anthraquinone is produced primarily for the manufacture of dyes and dye intermediates for use in the textile industry. There is a family of anthraquinone dyes.

9.1.7.10 Benzaldehyde. Benzaldehyde, which has an almond scent, is used largely in the manufacture of perfumes, flavor chemicals, dyes, and pharmaceuticals.

9.1.7.11 Benzoic Acid. Thirty-five percent of benzoic acid is used in plasticizers, such as stabilizers used in vinyl plastics. Eighteen percent is used to make sodium benzoate, which is used as a food preservative to prevent the growth of molds, yeast, and bacteria.

Benzoyl chloride accounts for 24 percent. It is an intermediate in the manufacture of benzoyl peroxide, a curing agent. Butyl benzoate, a dye carrier, accounts for another 8 percent. Alkyd resins, used in surface coatings, particularly on automobiles, account for 5 percent. Other substances, including food additives, drilling mud additives, medicines, flavors, and perfumes, account for the remaining 10 percent of benzoic acid consumption.

Benzoic acid is expected to have an average annual growth rate of between 6 and 8 percent.[27]

9.1.7.12 1,3-Butadiene. Seventy-six percent of butadiene consumption is in the production of elastomers. Styrene-butadiene rubber (SBR) accounts for 45 percent of the total consumption of butadiene. SBR, in turn, is used primarily for automobile and light truck tires as well as for hoses, belts, adhesives, and dipped goods.

Polybutadiene accounts for 20 percent of butadiene use. It also is used primarily (85 percent) in the manufacture of tires. Non-tire uses of polybutadiene include the production of polybutadiene-modified impact polystyrene.

Chloroprene/neoprene accounts for 8 percent of the butadiene total. Chloroprene is used to make neoprene, which is able to withstand considerable exposure to oil, heat, air, weather, and abrasion. Neoprene's main uses are in industrial and automotive items like hoses, belts, weather stripping, seals, gaskets, wire and cable coverings, construction, and adhesives.

Nine percent of butadiene use is in the manufacture of adiponitrile/hexamethylenediamine for the production of nylon 6,6 and nylon 6,12. Nylon 6,6 fibers are used in carpets, home furnishings, apparel, tire cord, and other uses. Nylon 6,6 plastics are used in injection molded gears and mechanical parts, including automotive parts. Nylon 6,12 plastics are used primarily in bristles and monofilament uses.

Seven percent of butadiene use is for styrene-butadiene copolymer latexes, especially for carpet-back coatings and paper coatings. Other uses include ABS plastics (6 percent) and various other uses including other polymers (2 percent).

Butadiene is projected to have an average annual growth rate of 2.5 percent through 1986.[28]

9.1.7.13 p-t-Butyl Benzoic Acid. p-t-Butyl benzoic acid is used in the manufacture of alkyd and other plastics and as an intermediate in the production of specialty chemicals.

9.1.7.14 n-Butyric Acid. n-Butyric acid is used in the manufacture of lacquers and plastics. It also is used in flavorings, plasticizers, pharmaceuticals, and leather tanning.

9.1.7.15 Crotonic Acid. Crotonic acid is used to produce a hot melt adhesive, in a copolymer with vinyl acetate, for bookbinding. It is used also in sizing, wood sealers, fungicides, butyric acids, and plasticizers.

9.1.7.16 Cumene Hydroperoxide. Cumene hydroperoxide is used primarily as an intermediate in the production of acetone and phenol. It is used also in peroxide catalyst applications and as a curing agent for vulcanizing rubber products.

Because cumene hydroperoxide is related directly to the production of acetone and phenol, it is assumed that it will have a similar average annual growth rate. This rate is between 4.0 percent (acetone) and 4.5 percent (phenol) (weighted by the amount of cumene hydroperoxide used for acetone and for phenol, the growth rate is computed to be 4.3 percent).

9.1.7.17 Cyclohexanol and Cyclohexanone. Ninety percent of cyclohexanol is used to produce adipic acid for the manufacture of nylon 6,6. The remaining 10 percent is used, to a large extent, for dyeing in the textile industry and producing cyclohexyl esters like dicyclohexyl phthalate. The phthalate esters are used primarily as plasticizers, particularly in heat-sealing coatings.

Forty percent of cyclohexanone is used to make caprolactam for the manufacture of nylon 6. Fifty-five percent is oxidized as mixed oil to manufacture adipic acid, which, as noted above, is used to manufacture nylon 6,6. The remaining volume of cyclohexanone is used mainly as a solvent for lacquers and crude rubber, spot removal, leather degreasing, and other solvent applications.

The average annual growth rate through 1986 should be tied to adipic acid, its main consumer, at a rate of 2.5 percent.[29]

9.1.7.18 Dimethyl Terephthalate (DMT) and Terephthalic Acid (TPA). DMT and TPA are used primarily in the manufacture of polyester fibers and film.

Polyester fibers account for 89 percent of DMT consumption and 95 percent of TPA consumption. Polyester film accounts for an additional 9 percent of DMT and 4 percent of TPA. Lesser uses of DMT include polybutylene terephthalate plastics.

Of the polyester fiber produced, apparel accounts for 62 percent, home furnishings for 17 percent, and other uses for the remainder. The manufacture of tire cord is a large use. Photographic film is the major use of polyester film. Polybutylene terephthalate plastics are used to replace automotive metal parts, often with glass fibers or mineral fillers. Polyethylene terephthalate barrier plastics are another use, as in carbonated beverage bottles.

DMT and TPA are projected to have an average annual growth rate of 7.5 percent through 1986.[30]

9.1.7.19 Ethylene Dichloride. Most ethylene dichloride is converted in nearby facilities to vinyl chloride, the raw material for polyvinylchloride.

Polyvinylchloride's largest market is construction. The polymer is used mostly for pipes and fittings; vinyl siding and home furnishings are additional uses.

Ethylene dichloride production is expected to grow at an average annual rate of 5.5 percent through 1986.[31]

9.1.7.20 Ethylene Oxide. Ethylene oxide is used in a number of applications. Sixty-four percent of ethylene oxide is used to make ethylene glycol, which is used as anti-freeze in automobiles and in making polyester fibers and films and other substances. Eleven percent of ethylene oxide is used for non-ionic surface active agents. Solvents like glycol ethers account for another 6 percent. Ethanolamines, which comprise 5 percent, are used in acid gas scrubbing, soaps, and detergents.

Diethylene glycol (5 percent of ethylene oxide consumption) is used to produce unsaturated polyester resins, textile lubricants and conditioners, plasticizers, and several other items. Triethylene glycol (accounting for 2 percent of ethylene oxide use) and diethylene glycol are used in natural gas dehydration. Triethylene glycol also is used as a humectant and in the manufacture of vinyl plasticizers.

Polyethylene glycol is used mainly in surface active agents and accounts for 2 percent of ethylene oxide use. The remaining 5 percent of ethylene oxide use is accounted for by miscellaneous uses.

The predicted average annual growth rate through 1986 for ethylene oxide is 3.5 percent.[32]

9.1.7.21 Formaldehyde. The majority of formaldehyde use involves the production of various plastics. Urea resins (25 percent), phenolic resins (24 percent), and melamine resins (4 percent) account collectively for more than half the total use of formaldehyde.

Other uses include pentaerythritol (6 percent), hexamethylenetetramine (4 percent), butanediol (8 percent), acetal plastics (7 percent), urea-formaldehyde concentrates (4 percent), chelating agents (4 percent), 4-4'-methylenedianile and 4-4'-methylenediphenyl isocyanate (3 percent), textile treating (2 percent), pyridine chemicals (1 percent), trimethylol-propane (1 percent), and other substances (7 percent) including nitroparaffin derivatives.

The largest uses of urea resins from formaldehyde are as adhesives in particleboards and fiberboards, as adhesives in other uses, and in molded plastic parts. Urea resins also are used in paper treating, coatings, and laminates.

Phenol-formaldehyde resins are used in bonding plywood and in binding various kinds of glass and mineral insulation. Acetal resins are used in automotive and appliance parts, plumbing hardware, and other items. Melamine-formaldehyde resins are thermosetting resins. Butanediol is used in making acetylenic chemicals, solvents, urethanes, polyesters, plasticizers, and elastomers.

The projected average annual growth rate through 1985 for formaldehyde is 4 percent.[33]

9.1.7.22 Formic Acid. Formic acid is used to dye exhausting agents for textiles, as a deliming agent and neutralizer for the leather industry, and as a chemical intermediate for various substances.

Formic acid is expected to have an average annual growth in production of 4 percent.[34]

9.1.7.23 Glyoxal. Glyoxal is used in the cross-linking of protein materials and in hydroxal-containing polymers. It also is used for shrinkproofing rayon and tanning leather and as a reducing agent in dyeing textiles.

9.1.7.24 Hydrogen Cyanide. The majority (62 percent) of hydrogen cyanide use is in the manufacture of methyl methacrylate. NTA and other chelates account for an additional 21 percent. Sodium cyanide, used mainly in the treating and electroplating of metals, accounts for 10 percent. Miscellaneous uses are involved in the remaining 8 percent.

The growth rate through 1986 for hydrogen cyanide is expected to be 6 percent per year.[35]

9.1.7.25 Isobutyric Acid. Isobutyric acid is used as a mercaptan solubilizing promoter in sweetening gasoline and in the manufacture of flavoring and perfume.

9.1.7.26 Isophthalic Acid. Isophthalic acid is used in making isophthalic polyester plastics (54 percent), which are used especially in glass fiber reinforced plastics such as corrosion-resistant equipment and pipe. It also is used in the manufacture of alkyd resins (26 percent) and other substances (24 percent), including dioctyl isophthalate plasticizer, polyester fibers and film, polyamide fibers, high-temperature-resistant polymers, electrical insulation resins, and hot melt adhesives. It also serves as a receptor in arimid fibers.

Isophthalic acid production is expected to increase at 7 percent per year through 1986.[36]

9.1.7.27 Maleic Anhydride. Fifty percent of the production of maleic anhydride is used in the manufacture of polyester plastics. Of the polyester plastics produced, three fourths are used in reinforced applications such as building panels, marine craft, marine accessories, and automobiles. The other fourth is used in casting plastics, putty resins, and clay pipe seals.

Fifteen percent of maleic anhydride is consumed in the production of fumaric acid. Ten percent is used in agricultural pesticides, including malathion, captan, and maleic hydrazide. Use in alkyd resins accounts for 5 percent. Miscellaneous applications account for the remaining 20 percent.

Maleic anhydride is expected to have an average annual growth in production of 5 to 6 percent through 1986.[37]

9.1.7.28 Methyl Ethyl Ketone. Methyl ethyl ketone is used primarily as a solvent. Its solvent applications account for the bulk of total use -- vinyl coatings solvent (34 percent), nitrocellulose coatings solvent (14 percent), adhesives solvent (14 percent), and acrylic coatings solvent (12 percent). Miscellaneous coatings account for 7 percent.

Lube oil dewaxing, by solvent extraction, uses 7 percent of all methyl ethyl ketone. Miscellaneous uses account for the remaining 6 percent, including solvent extraction in hardwood pulping and ink manufacture.

Methyl ethyl ketone is expected to have an average annual growth in production of 4 percent.[38]

9.1.7.29 Methyl Styrene. Methyl styrene is used in modified polyester and alkyd resin formulations. It also is used in food applications, paints, waxes, adhesives, and various plastics.

Methyl styrene is expected to have an average annual growth in production of 6 percent.[39]

9.1.7.30 Phenol. Forty-nine percent of phenol consumption is in the production of phenolic resins. The largest use for phenolic resins is in the plywood industry, where it is used to bond sheets of wood in producing plywood. Bisphenol A accounts for 14 percent of phenol use. The largest use of bisphenol A is the production of epoxy resins. Caprolactam accounts for 14 percent of phenol use and is used primarily to produce fibers and plastics.

Lesser uses of phenol include the manufacture of methylated phenol (4 percent), plasticizers (3 percent), adipic acid (3 percent), salicylic acid (2 percent), nonylphenol (2 percent), dodecylphenol (1 percent), other alkylphenols (3 percent), 2,4-D (1 percent), pentachlorophenol (1 percent), other chlorophenols (2 percent), petroleum refining (1 percent), and miscellaneous uses.

The predicted average annual growth rate through 1986 for phenol is 4.5 percent.[40]

9.1.7.31 Phthalic Anhydride. Phthalic anhydride use is oriented toward the plastic industry. Plasticizers, which account for 52 percent, are used mainly for polyvinylchloride. Dioctyl phthalates are the largest plasticizers.

Unsaturated polyester resins account for 22 percent of phthalic anhydride use. These are used as general purpose resins, particularly in the construction, marine, and synthetic marble fields.

Alkyd resins account for 21 percent of phthalic anhydride use. These resins are used as surface coatings. Phthalic anhydride is used to produce 80 percent of all alkyd resins.

Phthalic anhydride is expected to have an average annual growth in production of 3.8 percent.[41]

9.1.7.32 Propionic Acid. Propionic acid is used to a large degree in the agricultural sector. Its use as a grain preservative accounts for 38 percent of all propionic acid use. Calcium and sodium propionates, used as food preservatives, account for 26 percent. Propionic acid also is used to make herbicides. This use accounts for 13 percent. Ten percent of propionic acid is used in the manufacture of cellulosic plastics. Other uses, including pharmaceuticals, account for 13 percent.

Propionic acid is expected to have an average annual growth in production of 5 percent.[42]

9.1.7.33 Propylene Oxide. Propylene oxide is used primarily in the manufacture of plastics. Fifty-four percent of propylene oxide is used to manufacture polyurethane polyols. These are used to make polyurethane foams, which are used particularly in furniture and automobile seats, and non-foam plastics like surface coatings, elastomers, microcellular polyurethanes, and sealants.

Nineteen percent of propylene oxide is used to make propylene glycol, an intermediate in the production of unsaturated polyester resins. Three percent is used to make dipropylene glycol, also used in plasticizers and to make unsaturated polyester resins.

Two percent is used to make glycol ethers, which are used as solvents in the coatings industry. The remaining 22 percent of propylene oxide use involves miscellaneous substances, including non-urethane polyether polyols, glycerin, isopropanolamines, and other chemicals.

The predicted average annual growth rate through 1986 for propylene oxide is 5.5 percent.[43]

9.1.7.34 Styrene. Styrene is a high-volume plastic that has many end uses because of its relatively low cost and light weight. Eighty-one percent of styrene use is as polystyrene and styrene copolymers. These are broken down as follows: polystyrene, 62 percent; ABS and SAN resin, 10 percent; styrene-butadiene copolymer latexes, 7 percent; and other copolymers, 2 percent. In addition, 11 percent of styrene use is in the manufacture of SBR elastomers. Seven percent is used in unsaturated polyester resins; 1 percent is accounted for by miscellaneous uses.

Styrene's derivatives are, in turn, used in various functions. Polystyrene is used in packaging and construction markets. ABS resins are used in pipes, automobiles, and appliances. SAN resins, which are transparent rigid thermoplastics, are used in automobile instrument panel windows and lenses, clear housewares, and appliances. Styrene-butadiene copolymer latexes are used primarily as carpet back coatings and paper coatings. SBR elastomers account for the majority of elastomer use in passenger car and lightweight truck tires. Rubber products, such as industrial hoses and belts, and latexes for dipped products and adhesives are other uses of SBR elastomers. Unsaturated polyester resins and thermosetting resins are used mainly in fiberglass-reinforced plastics for marine, construction, and transportation items.

The ultimate uses of styrene and its derivatives are as follows: packaging, 22 percent; construction, 16 percent; electrical, appliance, television, communication, and office machines, 12 percent; households, 12 percent; transportation, 10 percent; recreation, 8 percent; disposable serviceware, 4 percent; exports, 5 percent; and miscellaneous uses, 11 percent.

The projected average annual growth rate through 1986 for styrene is 5 percent.[44]

9.1.8 Coproducts and Byproducts

A coproduct is essentially a chemical that is produced in conjunction with one or more other chemicals and is readily marketable; a byproduct is the "leftover" of the process, which, although in some cases is marketable, often is consumed captively. The concept of coproducts and byproducts is important because any cost of pollution control on the process would not be borne totally by an individual chemical.

If, for example, the cost of the cumene oxidation process increases, it may be passed on to the consumer in several ways. The coproducts of cumene oxidation are acetone and phenol. The increased costs may be passed on to acetone consumers and phenol consumers equally or if, say, the phenol market is stronger, 75 percent of the cost can be passed on to phenol consumers and 25 percent to acetone consumers. Conceivably, any combination is possible, but the exact ratio would depend on market conditions for the coproducts. Table 3-8 presents the AO chemicals that can be classified as coproducts.

The AO chemical byproducts, also listed in Table 3-8, all are recovered and used as intermediates in the production of other chemicals. They are not, however, the main end products of the process and any increase in production costs probably would be passed on (if market conditions allow it) solely through the primary chemical product. However, in the individual AO chemical economic analysis (Section 9.2), coproducts and byproducts are treated similarly. First, the cost of control is determined for an AO process, then all individual coproducts and/or byproducts produced by that process pass through the total cost of control (based on the primary chemical's smallest plant size) to demonstrate price inflation effects.

9.1.9 Growth in New Facilities

Forty-nine air oxidation chemical plant facilities are projected to be built between December 1, 1981 and December 1, 1986. The projection makes the critical assumption (Scenario I) that the capacity utilization rate in 1986 for each chemical will be equal to that chemical's average historical capacity utilization rate for the seven years preceding January 1, 1979. The average historical capacity utilization rate is a weighted average, with 1978 carrying the most weight and 1972 the least weight. Ideally, each chemical facility would operate at 85 percent of nameplate capacity over the long run. Many chemical industry sources state that, in the long run, 85 percent is about the maximum capacity achievable without putting a strain on plants. If all chemical facilities operated at 85 percent (Scenario II), the number of new facilities to be built would be 15. Given growth projections, present unused capacity, and the desire to operate at 85 percent capacity, there is not much room for new capacity (facilities).

The methodology for computing capacity increases and number of new facilities makes several key assumptions. First, all facilities have a life of 20 years, so that any new capacity built or added on to existing facilities between December 1, 1961 and December 1, 1966 would be retired during the five-year period examined in the analysis. The retired capacity would be replaced in order to satisfy existing and future demand and would fall under the category of modifications and reconstruction of existing facilities (see Section 5). Of course, all future modifications and reconstructions cannot be projected plausibly. Second, the size of the facility to be built for each chemical will be the same as the average size of present facilities used to produce that chemical. Finally, growth projections made through 1983 or 1984 are assumed to apply through 1986. Table 9-10 presents the equations for projecting the new capacity (facilities).

Results of the calculations are given in Table 9-11. As explained in the footnotes, byproducts and some coproducts are projected to have zero new facilities built because these chemicals are always produced in conjunction with other AO chemicals at the same facility. If acetone (a coproduct with phenol) was projected to have a certain number of new facilities based on the methodology given in Table 9-10 and if phenol also were projected to build new facilities, double counting would exist because phenol and acetone will be produced at the same new facility. The same situation exists for byproducts.

Of the two scenarios presented, Scenario I is the more realistic. An 85 percent capacity utilization rate (Scenario II) would be ideal economically for the producers but highly improbable. The average AO chemical capacity utilization rate has never reached 85 percent in the last 30 years. Historically, the capacity utilization rate usually has been around 80 percent for any given year, although the rate has fallen below 80 percent in the past few years. Unless demand makes an unusual and sharp increase, an 85 percent capacity utilization rate will not occur and a projection of 15 new facilities probably is too low. The best estimate is that 49 plants will be built between December 1, 1981 and December 1, 1986.

9.1.10 Substitution

Substitution is a prime variable when demand elasticity of an AO chemical is examined. If demand for a chemical is elastic because of substitute products, it is difficult to pass on increased costs to customers.

TABLE 9-10. EQUATIONS FOR PROJECTNG AO NEW CAPACITY AND FACILITIES
23 AO Chemicals
United States
Dec. 1, 1981 - Dec. 1, 1986

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1) $[FP (\frac{1}{CU}) - CC + RC - IC] \times AOP = NC$

2) $NC \div FS = NF$

where:

FP = "Future Production." For each individual chemical, the 1978 production figure is converted into a 1986 production figure based on a growth projection (see Section 9.1.7, "Individual AO Chemicals," for these growth projections).

CU = "Capacity Utilization." 1986 capacity utilization rates are expressed as a fraction. When Scenario I is used, the 1986 capacity utilization rate is based on the individual chemical's weighted average historical capacity utilization rate. These rates are listed below:

Acetaldehyde	0.74	Hydrogen cyanide	0.58
Acetic acid	0.89	Isophthalic acid	0.54
Acetone	0.73	Maleic anhydride	0.69
Acrylic acid	0.71	Methyl ethyl ketone	0.76
Acrylonitrile	0.87	a-Methyl styrene	0.81
Benzoic acid	0.69	Phenol	0.78
1,3-Butadiene	0.79	Phthalic anhydride	0.76
Dimethyl terephthalate	0.79	Propionic acid	0.44
Ethylene dichloride	0.73	Propylene oxide	0.76
Ethylene oxide	0.84	Styrene	0.83
Formaldehyde	0.69	Terephthalic acid	0.79
Formic acid	0.73		

Weighted capacity utilization rates are calculated by dividing the individual AO chemical's production by its capacity for each of the years 1972 through 1978. The 1978 capacity utilization rate is multiplied by 7, the 1977 rate by 6, the 1976 rate by 5, and so on down to the 1972 rate which is multiplied by 1. The products are added and then divided by 28 to arrive at the weighted capacity utilization rate. Production data are taken from U.S. International Trade Commision. Synthetic Organic Chemicals, US ITC Publication 10001. It is published each year. Capacity data are from SRI International, Directory of Chemical Producers and it is updated and published every year.

TABLE 9-10 (Continued). EQUATIONS FOR PROJECTING AO NEW CAPACITY AND FACILITIES
23 AO Chemicals
United States
Dec. 1, 1981 - Dec. 1, 1986

Scenario II presents the case where each individual chemical facility has an 85 percent capacity utilization rate in 1986.

CC = Current Capacity." See Table 9-2 for the 1978 total capacity for each chemical.

RC = "Retired Capacity." The useful life of an air oxidation facility is assumed to be 20 years such that the "retired capacity" figure represents capacity built between December 1, 1961 and December 1, 1966 and then rendered unproductive between December 1, 1981 and December 1, 1986. The 1961-1966 April and October issues of Chemical Engineering give a "Construction Alert" for all chemical facilities during that period that came on-line. Listed below are the individual chemical replacement capacity figures, which represents capacity added on in the years 1961-1966.

Acetaldehyde	45 Gg
Acetic acid	159 Gg
Acetone	75 Gg
Acrylic acid	0 Gg
Acrylonitrile	23 Gg
Benzoic acid	8 Gg
1,3-Butadiene	15 Gg
Dimethyl terephthalate	45 Gg
Ethylene dichloride	45 Gg
Ethylene oxide	179 Gg
Formaldehyde	205 Gg
Formic acid	0 Gg
Hydrogen cyanide	0 Gg
Isophthalic acid	27 Gg
Maleic anhydride	52 Gg
Methyl ethyl ketone	68 Gg
a-Methyl styrene	0 Gg
Phenol	150 Gg
Phthalic anhydride	107 Gg
Propionic acid	0 Gg
Propylene oxide	53 Gg
Styrene	204 Gg
Terephthalic acid	45 Gg

IC = "Interim Capacity." This represents capacity that is known to have come onstream or that is planned to come onstream after 1978 and before the date of proposal. The interim capacity information is found in in the 1978-1981 April and October issues of Chemical Engineering's "Construction Alert."

AOP = "Air Oxidation Proportion." This figure can be found in Table 3-7. In essence, it gives the probability (percent chance) that a new facility will be an AO facility.

NC = "New Capacity." This represents the estimated amount of new capacity in gigagrams that will be built between December 1, 1981 and December 1, 1986. This figure is rounded off to the nearest gigagram.

TABLE 9-10 (Continued). EQUATIONS FOR PROJECTING AO NEW CAPACITY AND FACILITIES

23 AO Chemicals
United States
Dec. 1, 1981 - Dec. 1, 1986

FS = "Facility Size." This represents the average facility size for each AO chemical. It is total capacity for the chemical divided by the number of facilities producing that chemical. Chemical capacities and facilities are given in Table 9-1.

NF = "New Facilities." This represents the number of new facilities to be built for each chemical during the first five years of the regulation. When the calculation is done, the number of new facilities is rounded of to the nearest whole number.

TABLE 9-11. PROJECTED NEW AO CHEMICAL FACILITIES BY CHEMICAL FOR TWO CAPACITY UTILIZATION SCENARIOS

23 AO Chemicals
United States
Dec. 1, 1981 - Dec. 1, 1986

Chemical[a]	Projected number of new facilities (scenario I)[b]	Projected number of new facilities (scenario II)[c]
Acetaldehyde	0	0
Acetic acid	2	1
Acetone	4	2
Acrylic acid	1	0
Acrylonitrile	0	1
Benzoic acid	3	1
1,3-Butadiene	1	1
Dimethyl terephthalate[d]	0	0
Ethylene dichloride	2	0
Ethylene oxide	1	0
Formaldehyde	19	5
Formic acid[d]	0	0
Hydrogen cyanide	4	0
Isophthalic acid	1	0
Maleic anhydride	6	3
Methyl ethyl ketone[d]	0	0
a-Methyl styrene[d]	0	0
Phenol[d]	0	0
Phthalic anhydride	3	1
Propionic acid	0	0
Propylene oxide	1	0
Styrene[d]	0	0
Terephthalic acid	1	0
TOTAL	49	15

TABLE 9-11 (Continued). PROJECTED NEW AO CHEMICAL FACILITIES BY CHEMICAL FOR TWO CAPACITY UTILIZATION SCENARIOS

23 AO Chemicals
United States
Dec. 1, 1981 - Dec. 1, 1986

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[a] This list of 23 chemicals represents only those chemicals for which projected growth rates, historical and current capacity and production data, and number of facilities are available. The other 13 chemicals are excluded for lack of such information and, in addition, are not especially essential to the new facilities projection. The 23 chemicals listed above represent approximately 95 percent of the total capacity that uses the AO process.

[b] Scenario I: The capacity utilization rate in 1986 for each chemical will be equal to the weighted average historical capacity utilization rate for that particular chemical

[c] Scenario II: The capacity utilization rate in 1986 for each chemical will be 85 percent of nameplate capacity. This is how full effective capacity utilization is defined.

[d] DMT is a coproduct of the TPA production process, methyl ethyl ketone and formic acid are byproducts of the acetic acid production process, a-Methyl styrene is a coproduct of the acetone production process, phenol is a coproduct of the acetone production process, and styrene is a coproduct of the propylene oxide process. The projected number of new facilities producing these chemicals is zero to avoid double counting.

AO chemicals are used ultimately as solvents, specialty chemicals such as flavors, fragrances, etc., or precursors in polymer or drug manufacture. For solvents, drugs, and specialty chemicals, chemical properties are most important. For polymers, precursors are chosen for a variety of mechanical, optical, electrical, and chemical properties.

When one characteristic is of predominant importance, a substitute usually can be found. This is the case with products used to produce drugs, solvents, or specialty chemicals. When a specific combination of properties is required, substitution is more difficult and sometimes impossible. This is the case for polymers used in plastics, rubbers, synthetic fibers, surface finishes, and adhesives.

Substitutes for the following AO chemicals conceivably could be found outside the AO industry:

- Acetaldehyde
- Acetonitrile
- Acrolein
- p-t-Butyl benzoic acid
- n-Butyric acid
- Crotonic acid
- Formic acid
- Glyoxal
- Hydroquinone
- Isobutyric acid.

Each of these chemicals, however, is used for several different purposes and there is no easily identifiable non-AO chemical that can be substituted for all of them. For example, acetaldehyde is used in the production of acetic acid, perfumes, plastics, and synthetic rubbers. It would be difficult to find one chemical that could serve as a substitute for acetaldehyde in all four uses.

The AO process may, in some cases, be substituted for by other types of processes. Table 3-7 demonstrates that 15 AO chemicals are known to be produced by non-AO processes. A few chemicals such as 1,3-butadiene, propionic acid, and styrene are produced mostly from non-AO processes. Economics and applicability determine whether one process, such as the chlorohydrin process, is competitive with the AO process.

9.1.11 Raw Materials

Raw materials represent the largest production cost for AO chemical producers. Table 9-12 gives the different raw materials used in producing AO chemicals. Note that AO chemicals acetaldehyde and acetic acid also are used as feedstocks. In addition, some raw materials are used to make more than one AO chemical. For more of a discussion of raw materials refer to Section 3.3.2.

The raw materials (listed in Table 9-12) are formed originally from either petroleum oil or natural gas, with oil the primary precursor of AO chemicals. Coal is not as yet a significant precursor. Compounds such as ethane, propane, naphtha, butane, and other single bond compounds are distilled from natural gas liquids and crude oil. Then, cracking the single bonded compounds yields some of the raw materials listed in Table 9-12 such as ethylene, the petrochemical produced in the largest volume, propylene, toluene and xylene. The remaining raw materials listed are formed either from the cracking of single bonded compounds or by the combination of two or more chemical compounds.

Almost all basic raw materials are interchangeable with each other and the choice of one particular compound as a raw material depends on economics. For instance, petrochemical producers presently are substituting propane and butane for high cost naphtha. Future raw materials prices are a major concern. The safest thing that can be said is that the prices of substitutable raw materials will alternate over the years. Thus, even though it is more expensive, new plants will be built with much greater raw material flexibility.

The current trend is toward using more crude oil and other heavy raw materials,[45] which will favor oil companies that have refineries. Also, there is an increasing interest in forming joint ventures between petroleum and chemical companies to produce large commodity chemicals. In such an arrangement, chemical companies are ensured a raw materials supply and large amounts of capital from the petroleum firms which, in turn, gain an outlet for their refinery products as well as an established marketing network.

Raw material prices will escalate substantially through 1986 due to rapidly rising oil and natural gas prices. The Department of Energy's

TABLE 9-12. RAW MATERIALS OF AO CHEMICALS
25 Raw Materials
United States
1978

Acetaldehyde
Acetic acid
Ammonia
Anthracene
Benzoin
n-Butane
n-Butyl alcohol
p-t-Butyl toluene
n-Butyraldehyde
Crotonaldehyde
Cumene
Cyclohexane
Diisopropylbenzene
p-diisopropylbenzene
Ethyl alcohol
Ethylbenzene
Ethylene
Ethylene dichloride
Ethylene glycol
Isobutyraldehyde
Methanol
Naphthalene
Propylene
Toluene
o-Xylene
p-Xylene

projections from the Midrange Energy Forecasting System show that the price of crude oil in 1986 will be $5.03 per gigajoule in 1978 dollars ($30.80 per barrel). This represents an average real annual increase of more than 20 percent. It is a substantial increase above and beyond general inflation and should mean large boosts in the price of downstream AO intermediate chemicals and their end products.

9.1.12 Prices

9.1.12.1 Price of AO Chemicals. The market prices for SOCMI chemicals produced by an AO process are given on Table 9-13. Anthraquinone, which is used to manufacture dyes, is the most expensive with a market price of 206.8 cents per kilogram. Formaldehyde is the least expensive of the SOCMI AO chemicals, with a market price of 11.2 cents per kilogram.

In chemical journals and periodicals, a list price is posted as the cost of a chemical. The list price is not the same as the selling price and is used only as a focal point around which actual selling prices are formed. Chemicals are sold on a contract price basis or a spot price basis, and chemical prices may be either greater or less than the current list price. Buying a chemical on contract guarantees the customer a supply for a predetermined price; this price usually has an escalator clause attached to account for inflation. The customer initially pays more than a market price for the guarantee of supply but may end up paying less if the chemical price outpaces inflation.

A spot price, or current market price, is determined by the market situation. Conventional supply and demand interaction is reflected when spot prices are quoted. The situation is similar to the sale of an automobile. The manufacturer sets a list price but the automobile usually is sold for less. The margin between what the car is sold for and the list price varies with the supply and demand situation. Most chemicals have a spot price that is below the list price; however, at times the spot price is greater than the list price because time is needed to set a list price (usually it is announced a month in advance) and a sudden tight supply situation may drive the spot market price above the list price.

9.1.12.2 Price Determination in the AO Industry. Given a specific demand for an AO chemical, different supply scenarios affect the selling price. If feedstocks are in short supply or are used for other priorities

TABLE 9-13. MARKET (SPOT) PRICES FOR AO CHEMICALS

36 AO Chemicals
United States
December, 1978

Chemical	Price (cents per kilogram)	Chemical	Price (cents per kilogram)
Acetaldehyde	39.7	Ethylene dichloride	18.1[a]
Acetic acid	33.3[a]	Ethylene oxide	49.2[a]
Acetone	35.9[a]	Formaldehyde	11.2[a]
Acetonitrile	91.3	Formic acid	40.6
Acetophenone	79.4	Glyoxal	73.4
Acrolein	70.3	Hydrogen cyanide	65.5
Acrylic acid	70.6[a]	Isobutyric acid	148.8
Acrylonitrile	50.7[a]	Isophthalic acid	58.7
Anthraquinone	206.8	Maleic anhydride	51.6[a]
Benzaldehyde	152.8	Methyl ethyl ketone	41.9[a]
Benzoic acid	52.9[a]	a-methyl styrene	39.7[a]
1,3-Butadiene	43.0[a]	Phenol	36.8[a]
p-t-Butyl benzoic acid	140.9	Phthalic anhydride	54.2[a]
n-Butyric acid	64.4	Propionic acid	37.5[a]
Crotonic acid	170.4	Propylene oxide	47.6
Cumene hydroperoxide	61.3	Styrene	39.7[a]
Cyclohexanol/cyclohexanone	73.4/72.8[a]	Terephthalic acid	50.5
Dimethyl terephthalate	47.0		

[a] This price is taken from U.S. International Trade Commission. Synthetic Organic Chemicals, United States Production and Sales, 1978. USITC Publication 10001. It represents an average unit value for the year 1978. It was assumed that this average unit value reflected an actual value for June 1978. This price was then made a December 1978 price by using the Bureau of Labor Statistics, Producer Prices and Price Indexes, December 1978. All other prices were calculated as 10 percent below their list price (the weighted-by-production-volume average of known market-list price differences). Prices are free on board (f.o.b.) plant or warehouse.

such as gasoline, then the selling price of the AO chemical should rise. This was the case during the Arab oil embargo that began in October 1973. If a large amount of new capacity comes on line, then price may be forced down; if an accident or strike should cause a plant to halt production, price should increase.

All AO chemicals are intermediate goods used in producing other goods and there may be a string of downstream products that build upon each other until a final end product is produced. Demand for an AO end product determines the demand for the AO chemical. Butadiene is used to produce styrene-butadiene-rubber (SBR), which is used in the production of tires, primarily for automobiles. Hence, the demand for automobiles and all the factors that determine this demand have repercussions all the way upstream, influencing the demand for butadiene.

The intersection of supply and demand curves represents the quantity purchased and sold at one price. The capacity utilization rate (production divided by total nameplate capacity) usually provides a good indication of the present interaction of supply and demand. For example, a low capacity utilization rate would mean that either too much had been supplied, or a slack in demand existed, or some combination of both. In other words, the price is too high to clear the market.

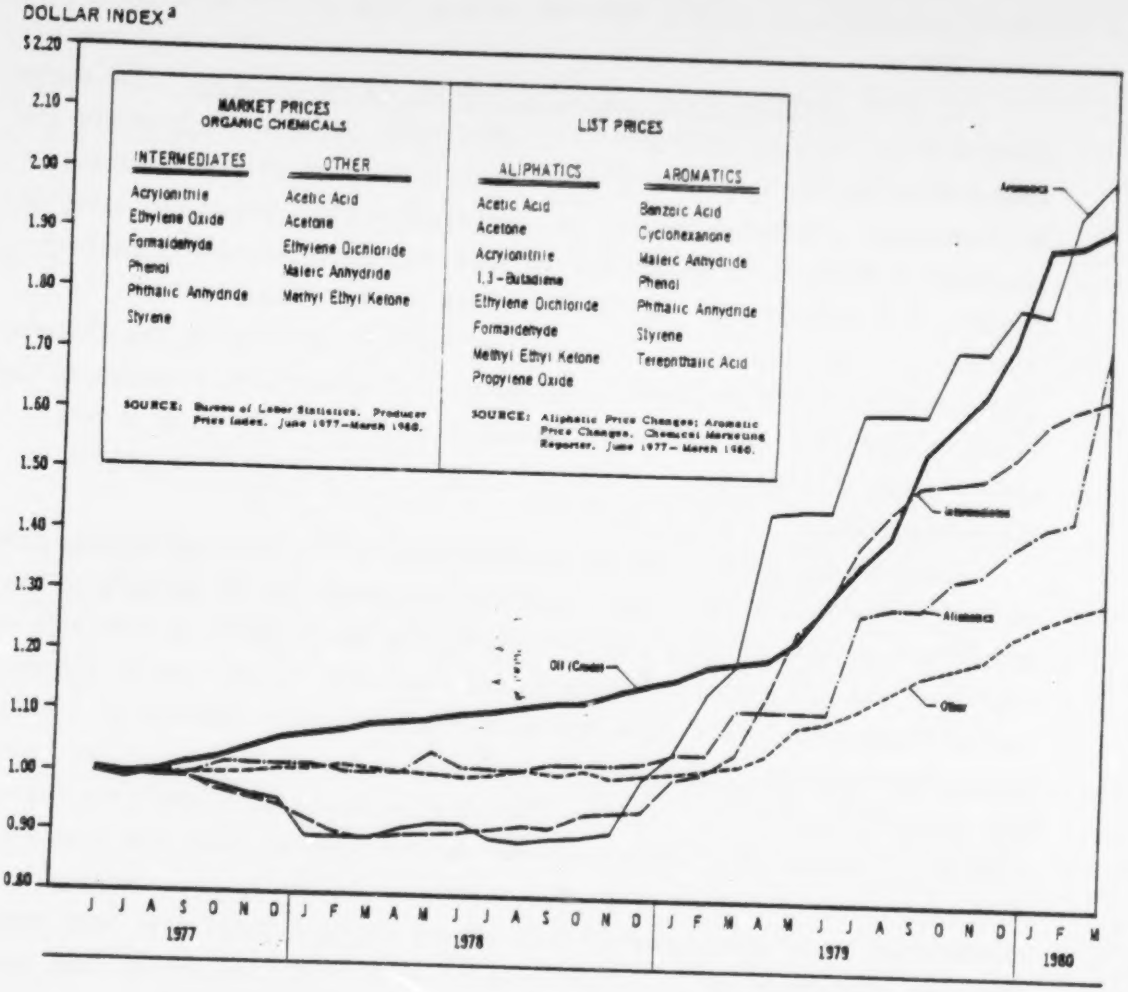
It would be difficult for a chemical producer to post a list price based on demand functions and elasticities. This is especially true with the AO chemicals since they are intermediate goods and all downstream demand functions must be considered. The AO chemical producers typically base their list prices on a full-cost, or cost-plus method. The full-cost pricing method involves adding a desired profit margin to estimated unit costs for a product price. Cost-plus pricing uses a percentage return on invested capital instead of a profit margin when calculating product price. This does not mean that demand elasticities are ignored. On the contrary, a lower margin is set if demand generally is thought to be elastic. Rigid profit margins are not the rule.

Historically, the price of AO chemicals has increased along with most everything else. The "real" price of these chemicals has been dependent upon the price of their main feedstocks. A "real" price is one that has been deflated by a general cost index (consumer's or producer's price index) and is given in nominal 1967 dollars. The real price of the AO chemicals increased greatly in 1974 as a result of the Arab oil embargo. From 1974 to the beginning of 1979, the "real" price generally declined for most of the AO chemicals, which means that prices increased at a slower pace than the general rate of inflation. During 1979, there were increases in the "real" price due to large increases in the cost of feedstocks. With recent deregulation of oil prices and deregulation of gas prices a probable future reality, the days of inexpensive feedstocks are numbered. AO chemicals should show rapidly rising "real" prices, at least through 1985.

The use of full-cost and cost-plus pricing implies that as costs increase, the price should increase at about the same rate. Because feedstocks comprise most of the production costs for AO chemicals, their prices should track very closely, as indicated by Figure 9-3. The figure shows price trends for various classifications of chemicals and for crude oil, the primary raw material feedstock in the production of AO chemicals. The aromatic (characterized by the presence of at least one benzene ring) and aliphatic (an open-chain structure consisting of paraffin, olefin, and acetylene hydrocarbons and their derivatives) trend lines represent changes in the list price. Since the end of 1978, it can be seen that producers have posted list prices that have either kept up with or exceeded the crude petroleum price increases. From December 1978 to March 1980, the cost of crude petroleum increased 67 percent. During the same time, the average list price for aromatics rose 100 percent, and for aliphatics, 67 percent.

Market prices, or the actual prices producers receive, as reflected in the "intermediate" trend line, also have matched the oil price increases (rising 75 percent between December 1978 and March 1980). However, AO chemicals included in the "other organic chemicals" category have risen relatively slowly. The composite market price for "other organic chemicals" has increased only 29 percent from December 1978 to March 1980.

If a severe economic slowdown does not come about, all chemical producers will be able to match raw material costs in the early 1980's.[46] This will be true if predictions of increasing capacity utilization for the chemical industry are accurate. Also, oil decontrol and gasoline conservation should ease the pressure on petroleum supplies and make feedstocks more readily available. This again confirms that the price of AO chemicals



SOURCE: Bureau of Labor Statistics. Producer Price Index. June 1977–March 1980.

SOURCE: Aliphatic Price Changes; Aromatic Price Changes. Chemical Marketing Reporter. June 1977– March 1980.

FIGURE 9–3. CRUDE OIL AND CHEMICAL MARKET PRICE INDEX AND LIST PRICE INDEX TRENDS

ORGANIC CHEMICALS

UNITED STATES

JUNE 1977–MARCH 1980

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[a] Based on a hypothetical price of $1.00 in June 1977 for all oil and chemical group classifications.

should increase more quickly than the general rate of inflation during the early 1980's.

9.1.12.3 Competitive Price Structure of the AO Industry. The market structure for most AO chemicals is oligopolistic because the products are homogeneous and the producers are not numerous. Five of the chemicals -- anthraquinone, p-t-butyl benzoic acid, crotonic acid, isobutyric acid, and isophthalic acid -- are exceptions in that they have only one producing company, a situation that may exist for one of two reasons. First, a chemical, its process, or its use may be patented, protecting the producer from competitors for 17 years. The second and more probable reason is that the five chemicals are specialty chemicals used captively or by a very select group of producers. Therefore, they yield little or no profit in the marketplace.

Each of the large volume AO chemical products is manufactured by five or more companies, with no one company owning more than 50 percent of the capacity. Pricing in this sort of competitive environment is difficult to label for the AO chemicals, although one term that can be used to characterize competitive price decisions is barometric price leadership.[47] The two relevant points to remember about barometric price leadership are that the identity of the price leader often changes and that leaders are not always followed. The producer who decides to raise or lower the list price first acts as a barometer of market conditions by making known through formal list price announcements that demand and cost conditions have changed. This new list price may be a confirmation of current spot prices that have departed significantly from the old list price. The leaders may not always be followed, particularly if they lack the market power to force the other producers into accepting their price decisions. Also, the other companies may adopt a "wait-and-see" strategy when one firm decides to change the list price.

Some chemical markets are more competitive than others. Acrylonitrile, which is produced by four companies that all have similarly sized plants, has a recent history of intense price competition. Price discounting has characterized the acrylonitrile market for some time. Price discounts, or temporary voluntary allowances (TVA) as they are known in the chemical business, usually amount to a 2.4 cents to 10 cents per kilogram undercut of the list price. Acrylonitrile producers have made numerous attempts in the past couple of years to eliminate these discounts and return prices to their list level. These attempts have failed due to the competitive nature of the acrylonitrile industry. During the summer of 1979, the list price of acrylonitrile was raised by approximately 4.5 cents per kilogram because of increasing demand and jumps in the price of the main feedstock, propylene. This constituted the first major price increase by acrylonitrile producers since the winter of 1976.

With full-cost pricing practices, oligopolistic coordination is enhanced because it makes the competitors' decisions more predictable. Such practices also provide common guidelines concerning what constitutes appropriate price levels. This is especially true if both the same costs pervade throughout AO chemicals production plants and the same full cost pricing rules are used.

A good example of pricing under barometric price leadership is the case of phenol, which is produced by 12 firms. Allied Chemical owns the largest single share of capacity, but only 17 percent of the total. The chronology of events below exemplifies the oligopolistic uncertainties of price setting.

Dow Chemical, which owns 14 percent of the total phenol capacity, announced in early September 1979 that it would raise its price 7.7 cents per kilogram on October 1,[48] bringing the list price to 83.6 cents per kilogram. Dow cited increased costs as the reason for raising its phenol price. Union Carbide had just boosted its price on phenol's feedstock, cumene, because of cost pressure from its feedstock, propylene.

The other chemical producers of phenol did not raise their prices immediately, taking the "wait-and-see" approach. Most suppliers need to notify customers of price changes only 15 days in advance.

By the end of September, all but two domestic phenol producers (Getty and Shell, 17 percent of total capacity combined) said they would post a list price of 83.6 cents per kilogram on October 1 in accordance with Dow's initial move. The week before, a large phenol seller said that it would post a TVA of 4.4 cents, making for an effective listing of 79.2 cents per kilogram, but by the end of the week had reconsidered and set a straight price of 83.6 cents per kilogram.[49]

Since Shell and Getty held back on increasing the price on October 1, the new 83.6 cents per kilogram price, which was implemented by the other producers, did not stick. All producers discounted the price to remain competitive. Then, in the middle of October, Shell and Getty notified their customers that they would boost the price of phenol to 83.6 cents per kilogram on November 1.[50]

Meanwhile, phenol buyers said that the 83.6 cents per kilogram price was too high and would not survive. They pointed out that the downstream users of phenol (it is mainly used as a resin) never experienced the tight markets that phenol sellers enjoyed earlier in the year and were never able to pass on the price hikes that took place at that time. Further, the 83.6 cents per kilogram price was considered unrealistic because an additional 302 gigagrams of phenol capacity (a 20 percent increase) were due to come onstream in the near future. Given the inability to pass on phenol price increases, the excess phenol capacity, and the raising of interest rates by the Federal Reserve Board that might adversely affect the important end-use markets of automobiles and housing, the price increase appeared not to have a chance.

By the end of October, Dow, which initiated the original price increase, was first to officially acknowledge the weakness of the phenol market and post a TVA. On November 1, the company's list price was discounted 4.4 cents per kilogram. The other phenol producers soon followed Dow's lead.

The phenol example exemplifies a number of characteristics of barometric price leadership and how AO chemical prices are set. First, the producer with the most production capacity is not necessarily the one that initiates a price increase or decrease. Second, price increases usually are based on costs, with the producer attempting to maintain a full-cost or cost-plus margin. Third, some producers may not follow a price leader's direction immediately, taking a "wait-and-see" strategy. Fourth, the use of temporary voluntary allowances is common and the list price usually is not the selling price. Fifth, supply situations (e.g., overcapacity) and downstream market demand conditions have an important effect on selling price and, at times, overrule the producer's full-cost or cost-plus pricing decision. Finally, the large volume AO chemical producers set prices non-collusively, but usually end up selling the product for the same price.

9.1.13 International Considerations

In 1978, the United States experienced a total trade deficit of $28.5 billion,[51] primarily because of the large amount of imported oil. Even though the oil import costs were reduced by $2.84 billion over 1977 costs, they still accounted for a $39.5 billion cash outflow in 1978.[52] Other sectors of the economy had a dismal international trade year in 1978 as well. The manufacturing sector ran a balance of trade deficit that was the largest in recent years. Automobiles, textile goods, and tires all had record deficits.

The biggest bright spot with regard to the United States manufacturing balance of trade is the chemical industry. With exports valued at $14.6 billion and imports at $7.1 billion, the chemical industry showed a net balance of trade surplus of $7.5 billion.[53] Exports in 1978 increased by $2.06 billion over 1977 exports. Imports also were on the rise, showing a $1.04 billion increase.[54] It is interesting to note that, since 1975, the U.S. balance of trade has shown a continual increase in its deficit (imports are rising at a faster rate than exports), while the chemical industry has experienced a continual increase in its trade surplus (exports are increasing at a faster rate than imports).

The International Trade Commission places individual chemical products into groups according to the Standard International Tariff Classification (SITC). All of the AO chemicals fall under SITC No. 512, entitled "Organic Chemicals." Organic chemicals make up about 25 percent of the total chemical industry's exports and imports. In 1978, $3.37 billion worth of organic chemicals were exported and $1.73 billion were imported for a total surplus of $1.64 billion.[55] This was a slight decline from the 1977 balance of trade surplus valued at $1.79 billion.

Table 9-14 shows imports and exports for major AO chemicals. 1,3-Butadiene is the largest valued import, representing 36 percent of the total dollar amount of organic imports. Styrene is the largest valued export, representing 23 percent of the total dollar amount of organic exports.

Most commodities produced by the chemical industry that use AO chemicals as production materials also experienced balance of trade surplus. Plastics and resins (SITC No. 581), a large customer for AO chemicals, had a surplus of $1.57 billion.[56]

TABLE 9-14. AO CHEMICAL EXPORTS AND IMPORTS
19 AO Chemicals
United States
1978

Chemical	Exports (Megagrams)	Imports (Megagrams)
Acetaldehyde	NA	4
Acetic acid	7,730	25,637
Acetone	54,710	630
Acrylic acid	4,605	NA
Acrylonitrile	135,036	1,501
1,3-Butadiene	NA	282,202
Dimethyl terephthalate	90,594	NA
Ethylene dichloride	310,582	NA
Ethylene oxide	34,719	427
Formaldehyde	10,448	1,107
Formic acid	3,200	NA
Isophthalic acid	1,985	NA
Maleic anhydride	1,309	3,535
Methyl ethyl ketone	15,517	24,773
Phenol	104,077	83
Phthalic anhydride	420	18,315
Propylene oxide	34,219	15,920
Styrene	358,045	13,982

NA = Information is not available.

SOURCE: U.S. Department of Commerce. U.S. Exports. Publication FT410. 1978.

Still, the United States ranked second to West Germany in 1978 as a chemical exporting nation, but this may change soon. U.S. chemical exports in 1979 are expected to have their best year yet, reaching from $16 billion to $17 billion. With imports estimated at $5 billion or less, the chemical industry may have a remarkable $12 billion trade surplus.[57]

The main reason for the large success of SOCMI exporters is the cost of feedstocks. In 1974, the Organization of Petroleum Exporting Countries restructured world oil prices in such a way that U.S. chemical producers have a large feedstock cost advantage over their foreign counterparts. More important, U.S. government oil and gas price controls serve as an indirect subsidy to American chemical producers and contribute heavily to the differences in international chemical prices.

The European Community is the hardest hit by feedstock cost differences. Europe is an important market, accounting for 28 percent of all chemical exports. Petrochemicals constitute a large portion of this total and they include SOCMI organic intermediates. In the United States, producers are able to sell these chemicals for two thirds the price of comparable European products. Table 9-15 shows price comparisons for some major AO chemicals.

U.S. chemical companies contend that government energy price regulations are not the main reason for the differences in chemical prices -- that better technology, economies of scale, and a better inter-plant distribution network all contribute to lower costs. The weakness of the dollar in the European market also contributes to the large price differences. In addition, chemical producers are quick to point out that the United States has an advantage due to feedstock flexibility. European producers have been dependent upon naphtha as their main feedstock. A severe shortage of naphtha resulted when Iranian oil supplies were cut off and the spot price of naphtha more than doubled within a year, causing the price of downstream chemicals to skyrocket. The Europeans particularly were hurt because Iran supplied 14 percent of their crude oil last year. However, it is hard to dispute the fact that the U.S. advantage in crude oil price, which is about $18.87 per cubic meter ($3.00 per barrel), is the main reason for chemical price differences.

The future, however, should improve for European chemical producers. Naphtha should become more available and European refineries are installing

TABLE 9-15. U.S. AND EUROPEAN PRICE DIFFERENCES FOR AO CHEMICALS
4 AO Chemicals
1979

Chemical	Relative prices[a] ($ per Mg)	
	U.S.	Europe
Styrene	495	605 - 620
Phenol	540	680
Terephthalic acid	460	620
Butadiene	460	530

[a] First-quarter 1979 dollars.

SOURCE: Chemical Industry Girds to Defend Exports. Chemical & Engineering News. P. 14. October 22, 1979.

additional capacity that has feedstock flexibility. The dollar should become stronger relative to European currencies, but this is difficult to predict. The big factor will be the deregulation of U.S. oil and gas prices, which should narrow considerably the chemical price difference between the United States and Europe.

Even though U.S. chemical exports to Europe may have reached the high water mark, the total amount exported still should remain fairly high for the next five years. Deregulation of U.S. oil and gas prices will be phased in and exports to other areas of the world should remain strong.

The United States is well protected from SOCMI imports by protective tariffs. This is especially true with regard to the benzenoid imports category, which contains many of the AO chemicals. Benzenoid includes any chemical whose molecular structure has one or more six-membered carbocyclic or heterocyclic rings with conjugated double bonds (e.g., the benzene ring or the pyridine ring). Until recently, tariff valuation for benzenoid chemicals was extremely protective under the American Selling Price (ASP) system. The ASP customs valuation system was implemented in 1922 and is applied only to those benzenoid imports that are labeled "competitive" with similar products made in the United States.

The ASP included both a specific duty (so many cents per kilogram) and an ad valorem duty (a percentage of the domestic price). For example, maleic anhydride in 1978 had a specific duty of 3.7 cents per kilogram and an ad valorem rate of 12.5 percent.[58] With a domestic price of 61.6 cents per kilogram, the tariff would amount to 11.4 cents per kilogram. This means that foreign competitors would face a tariff cost representing approximately 20 percent or more of their selling price, making it difficult for foreign producers to make a profit.

Recent multilateral trade negotiations conducted in Tokyo and Geneva have scrapped the ASP system and replaced it with a new set of tariffs that became effective on January 1, 1980. However, many benzenoid chemicals will be exempt from the new duty rates, having been withdrawn from trade negotiations. These benzenoid chemicals represented a $226 million portion of the $688 million in dutiable benzenoid imports during 1976.[59] The other benzenoid imports classified as "competitive" no longer would be dutied using the ASP system. Instead of applying an ad valorem tariff rate on the domestic price of the chemical, the rate is computed using the foreign invoice price. It was shown that maleic anhydride under the ASP system would have a tariff duty of 11.4 cents per kilogram. If the foreign invoice price was 11 cents per kilogram less than the U.S. price, the tariff duty would drop to 10.1 cents per kilogram. However, new tariff rates have been drawn up that protect these benzenoid chemicals almost as much as under the ASP system.

A tariff-cutting formula was implemented on chemicals other than benzenoids that cut high existing tariffs by a greater percentage than low existing rates. The average U.S. duty rate on dutiable chemical imports from non-communist countries was about 10.5 percent of domestic price before the trade negotiations were completed. This percentage has been lowered to slightly less than 7 percent of domestic price, representing an average reduction of 34 percent.[60] The average duty rate on imports from the European Community and Canada is now 7 percent, and from Japan, 7.5 percent. This is a reduction from the former average duty rate of 11 percent for European and Japanese imports and 13.5 percent for Canadian imports.

One of the major uses for the AO chemicals, resin and plastics, had import duties averaging 9 percent ad valorem before the trade pact. Now the average duty rate has been reduced to slightly more than 5 percent. Table 9-16 shows new tariff duty rates decided during the trade negotiations for some AO chemicals and some of the resin types that are produced using AO chemicals. The rates did not change substantially from the previous system.

Even though tariffs have been decreased in some instances by the recent trade pact, the AO chemical intermediates and their end-use chemical products are still very well protected. This is especially true for chemicals classified as benzenoid products. Chemical producers have lost very little ground in the recent trade negotiations, although certain concerns remain. One of these, price inflation, has been remedied by the tariff negotiations. Formerly, the tariff duty as a percentage of domestic price varied inversely with an increase in price, due to the use of a specific duty. For example, acetaldehyde had a specific duty of 3.3 cents per kilogram plus an ad valorem duty of 7.5 percent. In 1972, it sold for

TABLE 9-16. OLD, CURRENT, AND PROPOSED TARIFFS
6 Chemical Commodities
United States

Commodity	Old rate	Converted rate[a] (%)	Proposed treaty rate[b] ($)
Acetaldehyde	3.3¢/kg plus 7.5%	8.0	8.0
Ethylene glycol	3.3¢/kg plus 7.5%	15.8	12.0
Propylene glycol	3.3¢/kg plus 7.5%	12.8	11.5
Polyethylene resins	2.9¢/kg plus 10%	14.0	12.5
Acrylic resins	2.9¢/kg plus 10%	12.3	6.5
Melamine resins	2.9¢/kg plus 10%	13.6	7.0

[a] Effective January 1, 1980 (specific duty is converted to an *ad valorem* rate).

[b] After staged reductions over eight years.

SOURCE: Tariff-Rate Corrections. Chemical Week. P. 21. June 20, 1979.

about 19.8 cents per kilogram and the tariff duty amounted to 4.8 cents per kilogram (or 24 percent of the price). In 1978, acetaldehyde sold for 44 cents per kilogram. The tariff duty rose to 6.6 cents per kilogram, but this represented a much smaller percentage of the price (15 percent). Increasing prices mean smaller tariffs (in percentage terms); obviously, producers were concerned.

The new agreements have done away with specific duties. With only ad valorem rates, domestic price increases will not affect tariff incidence, which is a relief to chemical producers, especially in light of the rapid increases in oil prices recently.

Another problem that chemical producers face -- one that was not corrected by the trade agreement -- is the growing competition from government-operated plants. For example, 13 percent of the total world ethylene oxide capacity in 1976 was controlled by foreign governments. This share is expected to increase to 24 percent by 1983 based on known expansion plans.[61] The concern is that government-subsidized plants may not conduct business with a profit incentive in mind, but may instead consider full employment or a healthy balance of trade to be the prime objective.

On the export side, U.S. chemical companies have complained about the use of health and safety regulations to prevent imports from entering foreign countries. The new trade agreement has countries pledging not to use such regulations for the sole purpose of blocking imports. Violators of this pledge would face retaliatory trade bans.

Finally, and of particular relevance to this study, exporters are concerned with meeting environmental costs that their foreign competitors do not face. Although no specifics are available, Rep. Kenneth L. Holland (D, S.C.), a member of the House Ways and Means Committee, is suggesting "a delicately fashioned tax-relief code" that would not be labeled an export-subsidy measure to help chemical exporters.[62]

These problems do not seem major, however. Given the exclusion of many benzenoid products from the new trade pact, the relatively small decreases in most tariff rates, and the strong cost advantages AO chemical producers have over European competitors, the balance of trade for the chemical industry surplus should remain large through the next five years.

9.2 ECONOMIC ANALYSIS OF SOCMI AIR OXIDATION NSPS

9.2.1 Summary of the Economic Effects of the SOCMI Air Oxidation NSPS

Thirty-six air oxidation industries are examined for possible adverse economic effects due to the NSPS. It is estimated that if all new AO facilities are controlled, the maximum total annualized costs would be $67 million (before-tax 1978 $) in 1986. Also, it has been determined that no AO chemical price would increase by 5 percent or more due to the NSPS, that the decline in profitability would be insignificant, that chemical firms should be able to raise the needed capital to finance pollution control expenditures, and that any changes in foreign trade due to the standard would be minimal.

9.2.2 Economic Impact Analysis of the SOCMI Air Oxidation NSPS

The analysis of regulatory alternatives is based on the use of a single Volatile Organic Compound (VOC) control technique, thermal oxidation. Each regulatory alternative specifies a percentage reduction of national VOC emissions. Reductions will be achieved by requiring that a percentage of AO facilities use thermal oxidation to reduce waste stream VOC emissions. The regulatory alternatives range from a national VOC reduction of approximately 72 percent (the current baseline level) to a VOC reduction of approximately 99.4 percent from uncontrolled emissions (the highest level achievable using thermal oxidation at all AO facilities). The 1986 total annualized control costs for eight levels of national control are presented in Table 9-17; Figure 9-4 presents the calculations in graphic form.

The regulatory alternatives are established based on the concept of a total-resource-effectiveness (TRE) floor. Information concerning 59 existing facilities producing AO chemicals was used to construct a national statistical profile, which then was used to compute a TRE index. The index serves to distinguish between those affected facilities that would have to install controls and those that would not. An owner or operator of an affected facility with a TRE index below the chosen value (following final product recovery) would have to reduce VOC emissions by 98 percent or to 20 parts per million by volume (ppmv) by compound (measured by molecule instead of by atom), whichever is less stringent. TRE is a measure of the total resource requirement per unit VOC reduction associated with VOC control by

TABLE 9-17. FIFTH YEAR ANNUALIZED CONTROL COSTS
FOR SEVEN REGULATORY ALTERNATIVES
AND NATIONAL PERCENT EMISSION REDUCTIONS
Total Resource-Effectiveness Approach
United States
December 1, 1986

Regulatory alternative[a]	Facility TRE index cutoff[b]	Percentage of new sources affected[c]	Percentage emission reduction over baseline[a]	1986 total annualized control costs (10^6 1978 $)[d]
Baseline	0	0	0	0
I	0.7	7	31	3
II	1.5	14	46	7
III	2.2	19	57	11
IV	3.1	27	66	15
V	6.2	47	81	28
VI	6000.0	100	90	67

[a] The baseline regulatory alternative requires no control beyond current levels, except that modified SIP's, which reflect the RACT recommendations of the AO CTG, are assumed to be in force in ozone nonattainment areas requesting extension beyond 1982. Baseline refers to the degree of air pollution control currently required under typical SIP's. In addition, the baseline includes a CTG issued specifically to the states for controlling pollutant emissions from the AO process. The current baseline level is a 72 percent reduction from the uncontrolled level in national emissions from new sources. The remaining regulatory alternatives specify levels of control achieved by varying the percentage of all future AO facilities controlling VOC emissions. Seven representative alternatives are presented in this table. A more thorough discussion of the regulatory alternatives methodology is provided in Chapter 6.

[b] The TRE index of a facility is equivalent to the facility cost-effectiveness, multiplied by 100, and divided by $88.7 thousand/Mg. This $88.7 thousand/Mg value represents the highest facility cost-effectiveness of any vent stream in the national profile with a VOC concentration above the detectable limit. (The cut-off of 6000 associated with regulatory alternative VI reflects facilities that report vent streams with VOC concentrations below the detectable limit and, therefore, higher cost effectiveness.)

[c] The percentage of new sources affected when multiplied by 49 projected new sources will not work out to a whole number of new sources because percentages are based on 59 existing sources and are rounded.

[d] Total annualized costs for each regulatory alternative were calculated based on 59 existing AO plants and then multiplied by 49/59 to determine the total annualized costs for projected new AO plants. Costs, which are given in Chapter 8, are calculated for the year 1986, the fifth year after the standard is to be proposed.

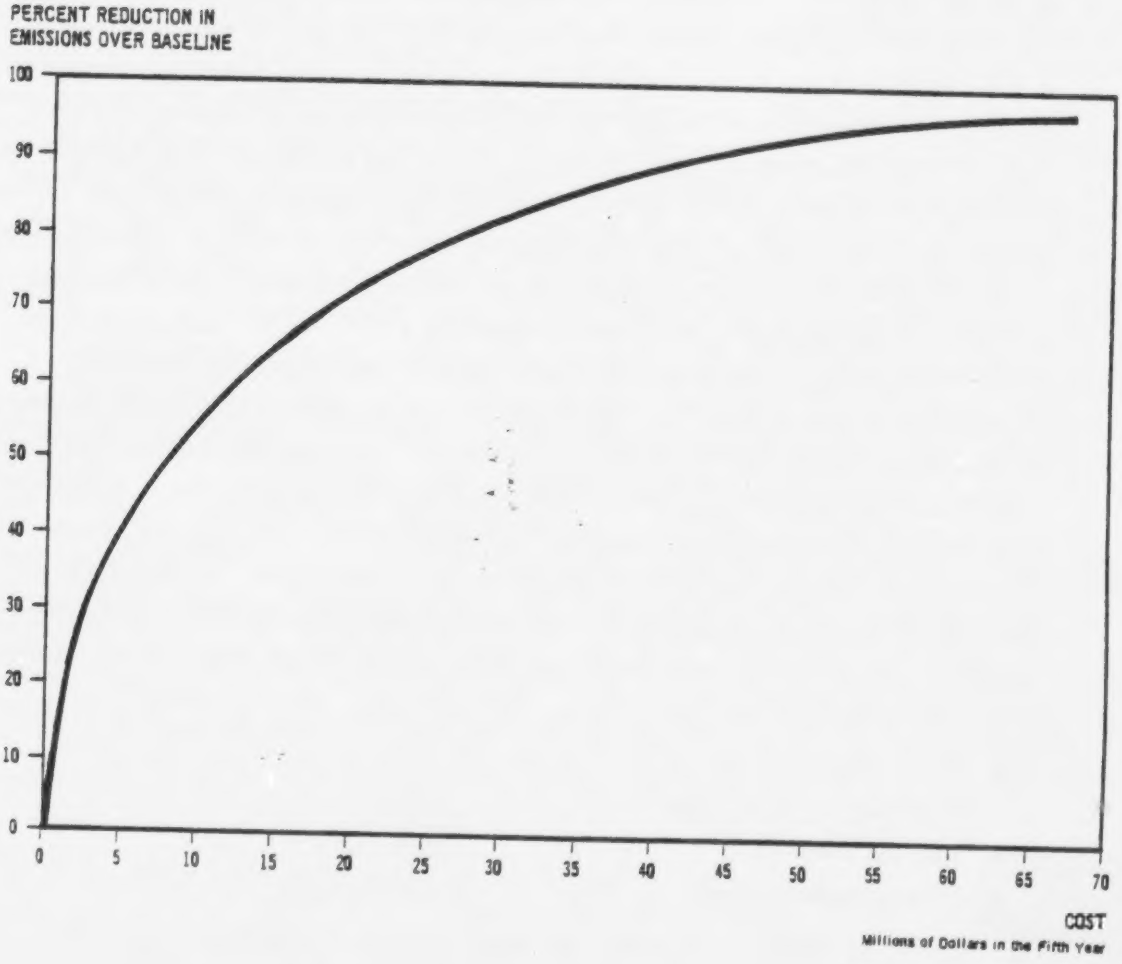

FIGURE 9-4. FIFTH YEAR ANNUALIZED CONTROL COSTS AND NATIONAL PERCENT EMISSIONS REDUCTION

TOTAL RESOURCE-EFFECTIVENESS APPROACH

UNITED STATES

DECEMBER 1, 1986

thermal oxidation. The TRE index of an affected facility is proportional to its projected annualized cost per unit VOC reduction (facility cost-effectiveness) associated with thermal oxidation at 98 percent control efficiency. The TRE index of a facility is equivalent to the facility cost-effectiveness, multiplied by 100, and divided by $88.7 thousand per megagram. The $88.7 thousand per megagram value represents the highest facility cost-effectiveness of any vent stream in the national profile with a VOC concentration above the detectable limit. (A more detailed discussion of how the regulatory alternatives are established is in Chapter 6.)

A detailed microeconomic analysis is not performed on each regulatory alternative because of the number of alternatives (seven) from which to choose and the number of different industries affected (36). Instead, the most stringent regulatory alternative is evaluated; hence, it is assumed that all future sources using the AO process will have to comply with the standard and reduce emissions by 98 percent or to 20 ppm by compound, whichever is less stringent. An economic screening analysis is conducted using four microeconomic criteria to ascertain whether any individual chemical industries would suffer adverse economic consequences. A "worst-case" approach defines the numerical thresholds that are used to screen out those industries that would not be affected significantly by the NSPS. If any one of the four screening criteria is triggered, the individual chemical industry is studied in more detail. The economic areas for which criteria are established include:

- Price increase
- Profitability decline
- Capital constraints
- Foreign competition.

The screening results are combined quantitatively to provide an overall ranking of the chemical industries. The ranking shows those chemical industries having the greatest potential for adverse economic effects from the NSPS.

The remainder of Section 9.2 describes the methodology used to implement the screening analysis, then presents both the results of the screening and the ranking of the 36 chemical industries in order of their potential for experiencing an adverse economic effect. Section 9.2 also examines more closely those chemical industries having the greatest potential for adverse economic effects. Section 9.3 describes aggregate and socioeconomic effects: total annualized cost, employment impacts, inflation resulting from the standard, and small business impacts.

The major conclusion reached is that there is little chance of major economic consequence for any of the 36 AO chemical industries due to the NSPS. The results indicate that, based on reduced profitability, a phenol facility might be built if the NSPS did not exist, but would not be built if the NSPS is imposed and if capacity utilization for the industry is low. However, the phenol industry impact due to the NSPS should not be overstated. The maximum price increase is projected to be only 0.9 percent in 1986 and the return on investment for the phenol producing process drops only 0.5 percent when control costs are imposed. Also, the only AO process producing phenol, the cumene hydroperoxide process, delivers acetone as a coproduct. Thus, control costs imposed on phenol may be shared with acetone.

9.2.3 Price Increase

This section attempts to estimate, for each of the 36 chemicals, the highest possible price increase caused directly by the AO NSPS. The price criterion states that if the worst-case annualized control cost in 1986 as a percentage of the projected 1986 price is greater than 5 percent for any chemical, that chemical industry should be scrutinized on a more detailed level. In many past government analyses, the 5 percent figure has been used as a generally accepted criterion for determining if a price rise is significant.

Certain conditions must be made explicit. Control costs are assumed to be passed through totally, without any decline in the quantity of the chemical demanded (i.e., the demand curve is assumed to be totally inelastic). It also is assumed that, in some cases, a return on the investment in control equipment exists due to heat recovery. Energy credits from the operation of the control equipment, expressed in monetary terms, are deducted from the control operating expenditures. When these conditions are met, control costs per unit produced, as a percentage of price per unit sold, are equivalent to a percentage increase in price due to the NSPS.

Any chemical industry whose maximum price increase is less than 5 percent is noted but not examined in depth in the price increase analysis. It is assumed that, given the worst-case parameters and a maximum price increase of less than 5 percent, the chemical's price rise would not cause any economic hardship downstream.

9.2.3.1 Price Increase Methodology. The cost of control is annualized using a capital recovery factor of 0.152, which represents an 8.5 percent after-tax interest rate and a 10-year life for the control equipment (control costs are presented in Chapter 8). The 8.5 percent after-tax interest rate is a real rate -- a 15.0 percent nominal after-tax rate adjusted by an assumed inflation rate of 6.0 percent.* An after-tax rate is used because it represents the actual opportunity cost to the investor.

In order to put the annualized control cost on a per kilogram product basis, the smallest existing facility size for a given chemical industry is used. This is equivalent to saying that any new facility built would be the same size as the smallest existing facility; this is a worst-case assumption because new facilities usually are larger on average than their predecessors and almost always are larger than the smallest existing facility. Where facility size data are not available, a 1.4 gigagrams per year production rate is used, representing the size of the smallest AO facility for which data are available (a hydrogen cyanide facility).

Projected 1986 market prices are used to compare the unit cost of control with unit price. Mid-year 1978 market selling prices (which may be found in Table 9-13) are used as the base from which 1986 prices are projected. The rise in the prices of SOCMI chemicals is expected to exceed the general rate of inflation. The use of full-cost and cost-plus pricing implies that prices should increase at about the same rate as costs. Because raw materials comprise most of the production costs for SOCMI chemicals, the price of the chemical and the raw material should track very closely.

The raw material most often used in the production process (either oil or gas) is determined for each chemical. Chemical prices are derived by escalating the 1978 market price by the projected percentage increase (in real terms) of each chemical's major raw material. In real terms, the price of crude oil is projected to increase by 146 percent from $2.04 per gigajoule ($12.50 per barrel) in 1978 to $5.03 per gigajoule ($30.80 per barrel) in 1986 (in 1978 dollars).[63] Gas prices are expected to increase 206 percent from $1.56 per gigajoule in 1978 to $4.74 per gigajoule in 1986 (in 1978 dollars).[64] The 1986 projected chemical prices are given in Table 9-18.

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*To convert a nominal interest rate to a real interest rate, one plus the nominal rate is divided by one plus the expected rate of inflation, and the result is subtracted from one.

9.2.3.2 Results of the Price Increase Screening. The price increase screening is carried out in three steps. First, an initial tabulation of control costs is generated using some worst-case assumptions. Two chemicals, made by three AO processes, experience price increases of greater than 5 percent: maleic anhydride via the benzene process (5.9 percent), maleic anhydride via the n-butane process (5.5 percent), and phthalic anhydride via the xylene process (5.3 percent).

The second step involves calculating a "rolling" cost. One of the 36 chemicals produced by an AO process, acetaldehyde, is used as feedstock for another AO chemical, acetic acid;[65] thus, the control cost per kilogram should be accumulated and divided by the price per kilogram of the downstream chemical. Accordingly, the downstream chemical's price should increase by more than its own control cost because it is passing on, in addition to its cost of control, the increased cost of feedstocks. A rolling cost is used in this instance to calculate the total effective percentage price increase of acetic acid resulting from its own VOC control plus the increased cost of acetaldehyde. A rolling cost does not force the acetic acid price over the 5 percent threshold. Results after the two steps are used as inputs for a ranking of the 36 AO chemical industries according to potential adverse economic effects (see Section 9.2.7).

The third step examines in more detail those chemicals that are found to have price increases of greater than 5 percent as determined in steps one and two. For maleic anhydride via the benzene process, maleic anhydride via the n-butane process, and phthalic anhydride via the xylene process, worst-case assumptions are replaced by more realistic assumptions and the price effects are reevaluated. Using more realistic control costs, maleic anhydride via the benzene process has a 4.2 percent price rise, maleic

TABLE 9-18. PROJECTED AO CHEMICAL PRICES IF EXPECTED INCREASES IN OIL AND NATURAL GAS PRICES ARE PASSED THROUGH
36 AO Chemicals
United States
December 1, 1986

Chemical	Price (¢/kg) (1978 $)
Acetaldehyde	97.7
Acetic acid	81.9
Acetone	88.3
Acetonitrile	224.6
Acetophenone	195.3
Acrolein	172.9
Acrylic acid	173.7
Acrylonitrile	124.7
Anthraquinone	508.7
Benzaldehyde	467.6
Benzoic acid	161.9
1,3-Butadiene	105.8
p-t-Butyl benzoic acid	346.6
n-Butyric acid	158.4
Crotonic acid	419.2
Cumene hydroperoxide	150.8
Cyclohexanol	180.6
Cyclohexanone	179.1
Dimethyl terephthalate	115.6
Ethylene dichloride	44.5
Ethylene oxide	121.0
Formaldehyde (100% solution)[a]	92.6
Formic acid	124.2
Glyoxal (100% solution)[b]	451.4
Hydrogen cyanide	200.4
Isobutyric acid	366.0
Isophthalic acid	144.4
Maleic anhydride	126.9
Methyl ethyl ketone	103.1
a-Methyl styrene	97.7
Phenol	90.5
Phthalic anhydride	133.3
Propionic acid	92.3
Propylene oxide	117.1
Styrene	97.7
Terephthalic acid	124.2

[a] Usually formaldehyde is sold as a 37% solution (37% formaldehyde, 63% water and methanol). The price of the solution is divided by 0.37 to obtain a 100% solution (pure formaldehyde) price because control costs are calculated on a 100% solution basis.

[b] Usually glyoxal is sold as a 40% solution (40% glyoxal, 60% water and methanol). The price of the diluted solution is divided by 0.40 to obtain a 100% solution (pure glyoxal) price because control costs are calculated based on a 100% solution basis.

anhydride via the n-butane process, 3.1 percent, and phthalic anhydride via the xylene process, 3.5 percent. The third step calculations are reiterated in Section 9.2.8 (Individual Chemical Analysis). Table 9-19 presents the results of the price increase calculations for all 36 chemicals that use various AO processes.

9.2.3.3 Sensitivity Analysis. The value of each of three control cost parameters is increased independently to determine if a chemical's percentage price change is sensitive to the individual parameter. The three parameters include: the interest rate used for discounting, the natural gas price in 1986, and the F value used to predict the actual offgas flow rate. In conducting the sensitivity analysis, two parameters are held constant while the third is being tested. As a result, this analysis only evaluates the sensitivity of the control cost to each parameter individually, and does not examine the combined influence of altering two or more of these factors simultaneously.

In the price increase analysis, an after-tax real interest rate of 8.5 percent is used. For the sensitivity analysis, an after-tax real interest rate of 10.8 percent is used. This is equivalent to a nominal after-tax interest rate of 23 percent divided by an inflation rate of 11 percent -- the approximate situation in late 1980 when the prime interest rate reached 21 percent, the highest level ever reached in the United States. When annualizing control costs using the 10.8 percent after-tax real interest rate, no significant increase in any chemical's price results when these control costs are passed through totally, nor do additional chemicals have price increases greater than 5 percent.

The price of natural gas is the main operating cost of control. However, the natural gas cost represents only a portion of the total annualized cost of control. The price of natural gas may prove to be less than the 1986 projected $4.74 per gigajoule (1978 $) used in the analysis. Also, because a few chemical prices are based on natural gas and because the price of gas is not totally independent of the oil price, the prices of all chemicals are linked to the gas price. If chemical prices also are lowered by the same rate as the natural gas price, control cost as a percentage of price (price increases) for all AO chemicals will be greater than the results provided in Table 9-19. A 1986 gas price of $4.12 per

TABLE 9-19. PERCENTAGE AO CHEMICAL PRICE INCREASES WHEN PRODUCERS PASS THROUGH ALL CONTROL COSTS

36 AO Chemicals, 29 AO Processes,
United States
December 1, 1986

Chemical[a]	Price Increase (%)
Acetaldehyde	1.8
Acetic acid (Wacker process)	3.2[b]
Acetic acid (n-butane oxidation process)	2.0
n-Butyric acid (byproduct)	1.9
Formic acid (byproduct)	1.3
Methyl ethyl ketone (coproduct)	1.6
Propionic acid (byproduct)	1.8
Acetone (cumene hydroperoxide process)	0.8
Acetophenone (byproduct)	0.4
Cumene hydroperoxide (byproduct)	0.5
a-Methyl styrene (byproduct)	0.8
Phenol (coproduct)	0.9
Acrylic acid	1.1
Acrolein (byproduct)	1.1
Acrylonitrile	1.3
Acetonitrile (byproduct)	0.7
Hydrogen cyanide (coproduct)	0.8
Anthraquinone	3.0
Benzaldehyde	1.9
Benzoic acid	2.7
1,3-Butadiene	3.8
p-t-Butyl benzoic acid	1.2
n-Butyric acid	1.9
Crotonic acid	0.6
Cyclohexanol	0.4
Cyclohexanone (coproduct)	0.4
Dimethyl terephthalate	1.1
Terephthalic acid (coproduct)	1.0
Ethylene dichloride	(0.3)
Ethylene oxide	1.0
Formaldehyde (mixed metal catalyst process)	3.0

TABLE 9-19 (Continued). PERCENTAGE AO CHEMICAL PRICE INCREASES WHEN PRODUCERS PASS THROUGH ALL CONTROL COSTS
36 AO Chemicals, 29 AO Processes,
United States
December 1, 1986

Chemical[a]	Price Increase (%)
Formaldehyde (silver catalyst process)	(1.4)
Glyoxal	2.1
Hydrogen cyanide (Andrussow process)	(2.9)
Isobutyric acid	1.0
Isophthalic acid	2.0
Maleic anhydride (benzene oxidation process)	4.2
Maleic anhydride (n-butane oxidation process)	3.1
Phthalic anhydride (xylene oxidation process)	3.5
Phthalic anhydride (napthalene oxidation process)	2.2
Propionic acid (propionaldehyde oxidation process)	0.7
Propylene oxide (ethylbenzene oxidation process)	0.8
Styrene (coproduct)	0.9

( ) = price decrease

[a] Chemicals that are coproducts or byproducts of a particular AO process are indented. A single value of capital cost, annualized cost, and operating cost is projected for such a process. In calculating the control costs for byproducts and coproducts, the total annualized cost for the process is attributed to each byproduct/ coproduct. Likewise, the total production of all byproducts and coproducts is used in calculating the control cost of each byproduct/ coproduct. Therefore, the control costs of the byproduct(s)/coproduct(s) are equal. Usually a pollution control cost will be passed on through the primary product and the price of the byproduct will remain the same and in the case of coproducts the price increase will be shared more or less equally. By using the above method for calculating control costs very conservative price increase results occur for byproducts and coproducts.

Some chemicals are produced by more than one AO process and thus have multiple price increases. Price rise differences may be a preliminary indication of possible process substitutions. Chapter 5 (Modification and Reconstruction of Existing Facilities) gives a current account of the types of AO processes used to make a chemical.

[b] 1.1 kg of acetaldehyde is used to produce 1 kg of acetic acid in the Wacker process. Hence 1.1 x control cost of acetaldehyde is added to the control cost of acetic acid to compute price increase.

gigajoule (1978 $) is used to determine if the chemical price increase would be substantially greater than that determined in the normal analysis. (The $4.12 per gigajoule 1986 gas price represents approximately the lowest Department of Energy projection.) The net result, when the $4.12 per gigajoule natural gas price is used, is no significant additional price increases when control costs are passed through totally. No additional chemicals have price increases greater than 5 percent, and it is concluded that the price increase is not very sensitive to changes in the price of natural gas.

The one parameter that produces the greatest disruption in the price increase conclusions is the F value. Because the actual flow rates for some chemicals are confidential, a statistical prediction formula for F is developed. The formula is the ratio of actual offgas flow rate to stoichiometric offgas flow rate. The screening methodology relies on control costs developed using the central predicted values of F. When a high value of F, based on the upper 95 percent confidence limit, is used to calculate control costs, the price increase due to the cost of control is significantly higher. Two additional chemicals experience a price rise of greater than 5 percent: anthraquinone (5.4 percent), and formaldehyde (metal oxide catalyst) (6.5 percent). Further economic examination of these two chemicals is not conducted in Section 9.2.8 due to the extremely conservative assumptions used when calculating the upper F value. The chance of the upper F value occurring is too small to warrant a detailed economic analysis for anthraquinone and formaldehyde. A detailed description of the F predictor is included in Chapter 8.

To summarize, the price increase screening analysis results are insensitive to the 1986 projected price of natural gas as well as the interest rate used to discount future prices. However, when an F value based on an upper 95 percent confidence limit is applied, price increases due to the cost of control become much greater than when a central value of F is used.

9.2.4 Profitability Decline

The key factor in the decision to build a new facility is whether the investment will be profitable. Profitability may be estimated by calculating the net present value (NPV) of future returns. Future returns are defined as the net income after taxes, plus depreciation, that result from an investment in a facility, and are discounted at the appropriate interest rate to calculate the NPV. If the NPV of a proposed facility is positive, the facility should be profitable; if negative, the facility would not be profitable. To determine if the additional costs of pollution control equipment will have adverse effects on investment decisions for SOCMI, NPV's are calculated for facilities with and without the control technology required by the regulatory alternative currently under consideration.

9.2.4.1 Profitability Decline Methodology. NPV calculations for SOCMI chemicals are based upon facility cost and sales estimates developed by Stanford Research Institute's (SRI) Process Economics Program. The facility data cover 12 AO processes representing an estimated 75 percent of the total number of AO processes to be used in projected new facilities from 1981 through 1986.* The data are considered proprietary.

The SRI facility cost data include the following estimates:

- Fixed investment -- the capital requirement for the facility and equipment in a new facility
- Total investment -- the sum of fixed investment plus inventory
- Product cost -- the cost of production (including depreciation) after deducting credits for byproducts. SRI's product cost assumes 100 percent capacity utilization; it has been adjusted to represent a facility running at a weighted average capacity utilization rate (see Section 9.1 for a discussion of how weighted average capacity utilization rates are figured).

The NPV formula for determining profitability, as well as a detailed explanation of how it works, is presented in Appendix A. Cash outflows are estimated on the basis of these three items and are stated in 1978 dollars. (All cost data were updated to 1978 using cost indices provided by SRI.) By using SRI facilities, a conservative assumption probably is made about profitability. Newly constructed AO process facilities should be more cost-efficient per unit produced than the existing facilities on which SRI bases its facilities. Also, the facility sizes used in calculating NPVs are at the smaller end of actual facility size range, while new plants are usually on the larger end of the range because firms try to capture economies of scale.

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*The 75 percent figure is obtained by dividing the number of new facilities projected to be built (see Section 9.1) using AO processes that the SRI data cover by the total number of projected new facilities.

Theoretically, depreciation is not treated correctly in the NPV calculation because of some simplifying assumptions that are made. In the NPV formula, SRI production quantities and costs are reduced to reflect historical capacity utilization rates for individual chemical facilities. In reducing costs, the depreciation included in costs also is reduced; this is not appropriate because depreciation is a fixed cost that does not vary with production volume. Thus, costs are understated and NPV's are overstated.

However, this simplification will not affect the NPV results significantly for two reasons. First, for many chemicals it is estimated from SRI data that depreciation is only about 10 percent of net production costs. This means that costs, when reduced to conform with historical capacity utilization rates, are understated by only to 2 to 4 percent. Second, all cost components, some of which include depreciation, are inflated annually at 13.2 percent in the NPV formula. This results in overstated costs and an understated NPV, more than offsetting the overstated NPV caused by the previously discussed cost-reducing simplification. The 13.2 percent overstatement of depreciable costs outweighs the 10 percent understatement of depreciable costs. Neither error makes a significant difference in the NPV result.

Cash inflows primarily are sales revenues estimated by multiplying the average unit price by the average annual production volume. 1978 prices are obtained from the International Trade Commission (see Table 9-13). Production volume is derived by assuming that a facility will run at the chemical's weighted average capacity utilization rate.

All NPV estimates are in 1978 dollars and assume that 1978 is the year in which an investment is made. Prices and costs are escalated from 1978 for 20 years (the life of the facility) at an annual rate of 13.2 percent. The total inflation rate chosen is based on a combined 6.0 percent annual general rate of inflation and a 6.8 percent annual real escalation rate derived from the DOE oil price projection to 1995. While it is impossible to forecast future inflation precisely, parallel indexing of both costs and prices in the NPV analysis will minimize any error from this factor.

Using the formula for the NPV calculations found in Appendix A to Chapter 9, two groups of NPV's are calculated: the baseline NPV's that reflect no additional investment requirements due to pollution control and NPV's for plants under the worst-case assumption that additional investment requirements and production costs imposed by the regulatory alternatives cannot be passed on to consumers of the product. Also assumed is that the quantity demanded of the product will not change. In the NPV formula, the control technology is replaced after 10 years.

The profitability screening criterion compares the NPV with and without control technology. A facility that maintains a positive NPV with emission controls remains an attractive investment to firms such that the NSPS would not negatively affect future construction of facilities. Also, a facility that has a negative baseline NPV would not undertake a new investment, thereby experiencing no major effect due to control costs. However, any facility with a positive NPV before controls and a negative NPV after controls is affected adversely and should be analyzed at a more detailed level for a better assessment of economic impact.

The NPV's are calculated initially at a 15 percent nominal after-tax interest (hurdle) rate. If an investment shows a positive NPV at 15 percent, any realistic interest rate used that is less than 15 percent also will give a positive NPV. This is true because the NPV is related inversely to the interest rate. A 15 percent nominal after-tax interest rate is fairly conservative when the general inflation rate is assumed to be 6 percent. One source of data on the cost of capital to industry stated that the real after-tax hurdle rate for organic intermediates ranged from 11.2 percent to 14.1 percent.[66] A more recent source, collecting data from a sample of 100 chemical manufacturing firms for 1977 and 1978, found that the mean real after-tax cost of capital is 10.8 percent with a minimum cost of capital of 8.1 percent and a maximum cost of capital of 12.8 percent.[67]

For any chemical process that has a negative baseline NPV using 15 percent, additional NPV's are computed using discount rates of 13.5 percent, 12 percent, 10.5 percent, and 9 percent. This is done to determine the rate at which the investment might change from a positive NPV without control costs to a negative NPV with control costs and to gauge the sensitivity of NPV to changes in the interest rate.

9.2.4.2 Results of the Profitability Decline Screening. Table 9-20 lists the NPV's for 12 AO processes used to produce nine SOCMI chemicals.

TABLE 9-20. NET PRESENT VALUES OF FUTURE FACILITIES, WITH AND WITHOUT POLLUTION CONTROL

9 AO Chemicals, 12 AO Processes, 15 Percent Interest Rate
United States
1986

Chemical[a]	Process[b]	NPV without controls (10^3 $)	NPV with controls (10^3 $)
Acetic acid	A)	- 9,125.6	- 13,346.6
	B)	41,967.3	36,080.7
Acetone	A)	91,890.0	87,574.6
1,3-Butadiene	A)	76,089.3	43,314.6
Ethylene oxide	A)	33,432.4	21,763.7
Formaldehyde	A)	64,716.2	58,340.4
	B)	58,697.8	67,735.7
Maleic anhydride	A)	- 6,304.7	-11,829.9
	B)	16,720.8	10,466.1
Phenol	A)	- 43,224.3	- 47,522.7
Phthalic anhydride	A)	19,492.6	11,897.6
Terephthalic acid	A)	- 35,349.8	- 49,482.0

[a] Net present values are calculated using SRI process cost data for different AO industries. The data are for one individual plant that may or may not represent an average plant for the particular AO industry. For instance, the process cost data for terephthalic acid show that it is an unprofitable investment at a 15 percent interest rate. However, the process cost data may represent a very small facility or a very old and uneconomical facility and not represent the "typical" terephthalic acid facility. A "typical" facility with a different set of process costs could prove to be very profitable. This may explain the discrepancy of projecting a future terephthalic acid facility when the NPV analysis shows that it would be a very unwise investment. Also, the fact that acetone, which has a positive NPV, and phenol, which has a negative NPV, are coproducts of the same cumene peroxidation process proves different economically oriented facilities are used in the NPV analysis.

[b] See Table 9-21 for a list of process descriptions.

(See Table 9-21 for a list of process descriptions.) As Table 9-20 shows, eight processes remain profitable at a 15 percent interest rate when producers fully absorb the cost of the pollution control equipment. Acetic acid (Wacker process), maleic anhydride (benzene oxidation process), phenol (cumene hydroperoxide process), and terephthalic acid (p-xylene oxidation process) all have negative NPV's with and without controls at a 15 percent interest rate. Table 9-22 gives a range of after-tax discount rates that change a profitable investment into an unprofitable investment when control costs are imposed.

Acetic acid (Wacker process) has a negative NPV without control costs at the lowest interest rate used, 9 percent. This implies that the facility is an unprofitable investment, even without control costs added, and would not be built. The formaldehyde facility using the silver catalyst process experiences a control cost credit because of heat recovery; thus control costs raise the net present value of the investment. Maleic anhydride (benzene oxidation process) is affected adversely by the additional costs of control at certain interest rates. By interpolation, at some point between a rate of approximately 9.6 percent and just below 9.0 percent, a profitable investment becomes unprofitable due to control costs.*

Phenol (produced by the cumene process) also has a negative NPV without control costs at the lowest interest rate used, 9 percent. This implies that the facility is an unprofitable investment, even without control costs added, and would not be built. Terephthalic acid (produced by the oxidation of p-xylene) also is affected. For a future terephthalic acid facility,

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*With the higher interest rate we equate the NPV without controls to zero and at the lower range of the interest rate we equate the NPV with controls to zero. For example, take the case of terephthalic acid A:

Interest Rate	NPV without Controls	NPV with Controls
12.0%	-18,095.7	-36,457.6
10.5%	- 5,938.2	-27,143.4
9.9%	0	
9.0%	9,539.9	- 15,171.8
<9.0%		0

Range: 9.9% - <9.0%

TABLE 9-21. AO PROCESSES
9 AO Chemicals
United States
1978

Acetic acid	(A)	Process:	Wacker (catalytic oxidation of acetaldehyde)
		Inputs:	acetaldehyde, catalyst, air
	(B)	Process:	oxidation of n-butane
		Inputs:	n-butane, air
Acetone	(A)	Process:	cumene peroxidation
		Inputs:	cumene hydroperoxide, sulfuric acid, air
1,3-Butadiene	(A)	Process:	Phillips (oxidative dehydrogenation of n-butenes)
		Inputs:	n-butenes, air, water, hydrogen, furfural or acetonitrile
Ethylene oxide	(A)	Process:	direct vapor-phase oxidation of ethylene over silver oxide catalyst
		Inputs:	silver, air, ethylene, steam, water
Formaldehyde	(A)	Process:	vapor phase catalytic air oxidation of methanol
		Inputs:	mixed metal catalyst, methanol, air
	(B)	Process:	vapor phase catalytic air oxidation of methanol
		Inputs:	crystalline silver catalyst, methanol, air
Maleic anhydride	(A)	Process:	oxidation of benzene
		Inputs:	air, benzene, sodium perborate, demineralized water
	(B)	Process:	oxidation of n-butane
		Inputs:	n-butane, air, catalyst
Phenol	(A)	Process:	cumene peroxidation
		Inputs:	cumene hydroperoxide, sulfuric acid, air
Phthalic anhydride	(A)	Process:	air oxidation of o-xylene in a fixed catalyst bed reactor
		Inputs:	o-xylene, air
Terephthalic acid	(A)	Process:	air oxidation of p-xylene in the liquid phase
		Inputs:	p-xylene, air, acetic acid

TABLE 9-22. HURDLE RATES AT WHICH NET PRESENT VALUES OF FUTURE FACILITIES CHANGE FROM POSITIVE (WITHOUT POLLUTION CONTROL) TO NEGATIVE (WITH POLLUTION CONTROL)

4 AO Chemical Processes
United States
1986

Chemical process[a]	After-tax nominal hurdle rate (%)
Acetic acid A:	<9b
Maleic anhydride A:	<9-9.6
Phenol A:	<9[b]
Terephthalic acid A:	<9-9.9

[a] See Table 9-21 for a list of process descriptions.

[b] Acetic acid (Wacker process) and phenol (cumene process) show a negative baseline NPV when a 9% after-tax interest rate is employed.

an interest rate between 9.9 percent and less than 9 percent results in an unprofitable investment.

9.2.4.3 Profitability Decline Sensitivity Analysis. When a sensitivity analysis is done on those processes listed in Table 9-21, raising the values of the natural gas price and the F ratio independently, no additional chemical processes are affected under the profitability decline criterion. A sensitivity analysis on the interest rate used for discounting is included in the NPV screening analysis presented in Section 9.2.4.1 with results given in Section 9.2.4.2.

9.2.5 Capital Constraints

The ability of a firm to raise capital to finance incremental control costs is an important consideration in determining the economic impact of a SOCMI NSPS. It is conceivable that a firm would find a new facility investment profitable, even with control costs added, but may not be able to raise the extra capital needed to purchase pollution control equipment. This is one of the most difficult impacts to measure because there are few direct data upon which to draw. To identify potential problems, the magnitude of the capital costs of the control technology relative to the fixed investment costs without control is examined. There is no screening mechanism for readily identifying chemical industries that may have trouble raising capital. Of the 12 model processes examined, the one with the highest capital control cost-to-fixed facility investment ratio is analyzed further for adverse economic effects. A 1,3-butadiene facility has the highest ratio. It also is the only one with capital costs of control exceeding 20 percent of the facility's fixed investment costs. The 20 percent figure should not be construed as either an absolute or relatively significant threshold, but a cost analysis manual states that contingency costs -- the excess account set up to deal with uncertainties in the cost estimate, including unforeseen escalation in prices, malfunctions, equipment design alterations, and similar sources -- are about 20 percent of total direct and indirect costs.[68] This implies that firms are either prepared or already possess the ability to finance costs that range 20 percent above any investment they choose to undertake.

The 1986 estimated capital cost of control converted to 1978 dollars (refer to Chapter 8) is divided by the fixed investment costs taken from

SRI's Process Economics proprietary information. It is assumed that a replacement incinerator is not considered when a firm decides to make an up-front capital outlay and that the capital control cost of the first incinerator should not be added to the NPV of a second incinerator and then divided by the fixed investment.

9.2.6 Foreign Competition

9.2.6.1 Foreign Competition Methodology. Imports and exports are important variables to examine in this analysis because the emission standard is placed only on domestic plants. If domestic producers raise their prices because of the extra cost of controlling pollution, they may be at a competitive disadvantage with their foreign counterparts. Chemical exports may suffer a decline if foreign customers substitute organic chemicals from other countries. Also, imports from foreign countries into the United States may increase, causing an adverse effect on our balance of trade.

The foreign competition criterion is defined such that any chemical industry having imports and/or exports exceeding 10 percent of its total U.S. production is examined further. The 10 percent figure is fairly conservative when considering the importance of the foreign market as part of the total market.

Fifteen chemical industries having import data available are examined to see if imports in 1978, as a percentage of 1978 domestic production, exceed the screening threshold figure of 10 percent (see Table 9-23). Only two chemical industries, 1,3-butadiene and methyl ethyl ketone, fail the screen and are examined further for possible adverse international economic impacts. Of the 17 AO chemical industries that have export information available, three fail the screen: acrylonitrile, styrene, and formic acid.

9.2.6.2 Results of the Foreign Competition Screening. It is important to note that increases in costs due to emissions control do not influence changes in the future balance of trade. Other overriding factors will influence the SOCMI AO chemicals' position in the world market. As the United States phases out oil and gas price controls, U.S. companies will face higher feedstock prices that reflect the higher world oil price. Therefore, the U.S. feedstock cost advantage will be eliminated, causing a decline in the net balance of trade surplus. The chemical industries that have significant levels of foreign trade (greater than 10 percent of domes-

TABLE 9-23. IMPORTS AND EXPORTS AS A PERCENTAGE OF PRODUCTION*
19 AO Chemicals
United States
1978

Chemical	Imports	Exports
Acetaldehyde	b	NA
Acetic acid	2.0[c]	0.6[c]
Acetone	0.8[c]	5.7[c]
Acrylic acid	NA	3.5[c]
Acrylonitrile	0.2[c]	17.0[a,c]
1,3-Butadiene	17.3[a,c]	2.9[f]
Cyclohexanol/Cyclohexanone	b,c	b,d
Dimethyl terephthalate/ Terephthalic acid	b,d	3.4[c]
Ethylene dichloride	NA	6.2[c]
Ethylene oxide	b,c	1.6[c]
Formaldehyde	b,e	0.4[c]
Formic acid	NA	11.7[a,c]
Isophthalic acid	NA	3.2[c]
Maleic anhydride	2.7[c]	0.9[c]
Methyl ethyl ketone	10.8[a]	5.7[c]
Phenol	0.2[c]	8.4[c]
Phthalic anhydride	5.7[c]	NA
Propylene oxide	b,f	3.7[c]
Styrene	0.5[c]	11.4[a,c]

*Quantities are by volume; percentages are of total production by each chemical

NA = Not available

[a] Affected chemical industries

[b] Less than 0.05 percent

[c] U.S. Department of Commerce. Import Information was taken from "Benzenoid Chemicals - Imports 1978"; Export information was from Publication FT410, Schedule B.

[d] Chemical and Engineering News. P. 11. March 26, 1979.

[e] Chemical and Engineering News. P. 14. January 22, 1979.

[f] Chemical and Engineering News. P. 13. July 24, 1978.

tic production) all have a small cost of control relative to their 1986 projected price (less than 5 percent). These chemical industries are discussed below in more detail.

1,3-Butadiene. In 1978, the amount of imported 1,3-butadiene equalled 17.3 percent of domestic production. The United States has been a net importer of 1,3-butadiene since 1968.[69] The quantity of imported 1,3-butadiene is tied closely to the demand for rubber and, therefore, the demand for tires. In 1976, the rubber workers' strike resulted in decreased demand for 1,3-butadiene and the closing of older facilities. Also, smaller cars and radial tires have had an adverse effect on demand. These factors have led producers to undertake new investments cautiously with the result that the United States is unable to produce sufficient quantities to meet domestic demand. In 1978, while U.S. facilities averaged 85 percent capacity utilization (full capacity for this industry) the United States imported 282 gigagrams of 1,3-butadiene.

The origin, quantity, and value of 1978 1,3-butadiene imports are listed in Table 9-24. The largest exporters to the United States were the Netherlands and the United Kingdom, which together accounted for more than two thirds of total imports. There is no duty on 1,3-butadiene imports; therefore, the United States is expected to remain a net importer of 1,3-butadiene.

The cost of control for 1,3-butadiene is estimated to add a maximum 4.0 cents per kilogram, representing 3.8 percent of the 1986 projected price. Growth in demand is expected to be slow (2.5 percent per year); therefore, a 3.8 percent or smaller increase in after-tax cost will not affect significantly the U.S. position in the international 1,3-butadiene market.

Methyl Ethyl Ketone. Import levels of methyl ethyl ketone in 1978 reflect the tight supply that characterized the market in that year. New capacity has come onstream since 1978 and has resulted in an export volume that appears to be well above imports in 1979.[70] The cost of control for methyl ethyl ketone is estimated to be 1.5 cents per kilogram. Although the quantity of imports is decreasing, the standard's cost is insignificant (1.6 percent of 1986 selling price) and will not influence trends in foreign trade.

TABLE 9-24. 1,3-BUTADIENE IMPORTS BY COUNTRY OF ORIGIN
United States
1978

Country	Quantity (Gg)	Value (10^6 $)
Netherlands	123.7	53.4
United Kingdom	70.6	30.0
France	30.3	12.6
Italy	17.1	7.0
Japan	13.7	5.9
West Germany	12.3	5.2
Norway	4.3	1.6
Brazil	3.1	1.5
Belgium	1.8	30.8
Taiwan	1.0	0.4
All Others	3.0	1.4
TOTAL	282.0	119.8

SOURCE: U.S. Department of Commerce. United States General Imports Schedule A Commodity By Country FT/1351. December, 1978.

Acrylonitrile. In 1978, exports of acrylonitrile exceeded 15 percent of total U.S. acrylonitrile production. The quantity of exports was approximately 134.7 gigagrams, valued at over $60 million.[71] More than one third of these exports went to Canada and Mexico; western hemisphere countries accounted for more than 60 percent of the total exported volume.

United States acrylonitrile producers have done well in foreign trade due to their feedstock cost advantage. The contract price for propylene in the first quarter of 1979 was one third greater in Europe than in the United States (see Table 9-25). The cost of control for acrylonitrile is estimated to be, at most, 1.5 cents per kilogram, representing 1.3 percent of the 1986 projected price. This small increase in cost, due to control, should not affect significantly the ability of U.S. producers to compete in the world market.

Styrene. In 1978, the United States exported approximately 357.3 gigagrams of styrene valued at $127 million. Styrene, a benzenoid derivative, still is protected by tariffs despite recent tariff reductions. The feedstock price advantage held by U.S. producers explains the magnitude of exports. Benzene and ethylene, the feedstocks for styrene, are priced 17 percent and 65 percent greater, respectively, in Europe than in the United States (see Table 9-25).

The cost of control is estimated to be 0.9 percent of the projected 1986 price of styrene; this increment should not affect the ability of U.S. manufacturers to compete in foreign markets given the small percentage increase in total cost and the large raw material advantage.

Formic Acid. Exports account for 12 percent of total domestic production of formic acid. Compared to acrylonitrile and styrene, formic acid is a low volume chemical. U.S. producers exported only three gigagrams of this chemical.

The cost of control for formic acid is estimated to be 1.3 percent of the projected 1986 price. This is a small cost increase and would not effect the level of exports of this chemical severely.

9.2.7 Ranking of Chemicals

A ranking scheme is developed to combine the various effects of the NSPS on the SOCMI AO chemicals. The chemical industries ranked highest are examined in more detail in Section 9.2.8 of the analysis for potential

TABLE 9-25. CHEMICAL FEEDSTOCK PRICES
3 Feedstocks
United States vs. Europe
1978

Feedstock	Relative prices[a] ($/metric ton)	
	U.S.	Europe
Benzene (contract)	285-330	360
Ethylene (contract)	285	470
Propylene (contract)	200	300

[a] First Quarter 1979

SOURCE: Chemical Industry Girds to Defend Exports. Chemical and Engineering News. P. 14. October 22, 1979.

adverse economic effects. The scheme assigns values to the AO chemical industries based on their criterion test results.

- Inflation criterion (price, P)

  Let P = 4 times the inflation calculation (inflation calculated after after steps 1 and 2 of the price increase screening -- see Section 9.2.3.2)

- Profitability criterion (net present value, NPV)

  Let D = the percentage decrease (or increase) in the net present value due to control*

  Let NPV = 1.0 if $0 \leq D < 10$
  Let NPV = 1.5 if $10 \leq D < 20$
  Let NPV = 2.0 if $20 \leq D < 30$
  Let NPV = 2.5 if $30 \leq D < 40$
  Let NPV = 3.0 if $40 \leq D < 50$
  Let NPV = 3.5 if $50 \leq D < 60$
  Let NPV = 4.0 if $60 \leq D$

  If there is an increase in the net present value due to the control, the value assigned NPV was multiplied by -1. An increase in net present value is a positive effect of the standard and appears as a credit in ranking.

- Capital Availability Criterion (C)

  Let C = 0.5 of the capital availability calculation (capital cost of control divided by the facility's fixed investment, multiplied by 100; data used in this calculation are proprietary)

- Foreign competition (F)

  Let F = 0 if the inflation calculation is less than 5
  Let F = 0.3 of foreign competition calculation if the chemical fails the price screen

- RANKING SCORE = P + NPV + C + F.

Table 9-26 presents the ranking of the AO chemicals. The values assigned to the tests reflect their importance in the screening study used

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*The percentage decrease (increase) in the net present value =

$$100 \left[\frac{\text{(Decrease (or Increase) in net present value due to control)}}{\text{net present value before control}}\right]$$

Numbers for the calculation are obtained from Table 9-20.

TABLE 9-26. CHEMICALS RANKED BY POSSIBLE ECONOMIC EFFECTS OF AO NSPS*

36 AO Chemicals, 29 AO Processes
United States
1978

Rank	Chemical	Score
1	1,3-Butadiene	27.7
2	Maleic anhydride (benzene oxidation process)	24.2
3	Phthalic anhydride (xylene oxidation process)	22.8
4	Formaldehyde (mixed metal catalyst process)	21.2
5	Maleic anhydride (n-butane oxidation process)	21.0
6	Acetic acid (Wacker process)	12.8
7	Anthraquinone	12.0
8	Acetic acid (coproduct with methyl ethyl ketone via n-butane oxidation process)	10.8
	n-Benzoic acid	10.8
10	Phthalic anhydride (naphthalene oxidation process)	8.8
11	Glyoxal	8.4
12	Isophthalic acid	8.0
13	n-Butyric acid (byproduct of acetic acid via n-butane oxidation process)	7.6
	Benzaldehyde	7.6
	Phenol (coproduct wth acetone via cumene hydroperoxide process)	7.6
16	Propionic acid (byproduct of acetic acid via n-butane oxidation process)	7.2
	Acetaldehyde (Wacker process)	7.2
18	Terephthalic acid (coproduct with dimethyl terephthalate)	6.8
	Ethylene oxide	6.8

TABLE 9-26 (Continued). CHEMICALS RANKED BY POSSIBLE ECONOMIC EFFECTS OF AO NSPS*
36 AO Chemicals, 29 AO Processes
United States
1978

Rank	Chemical	Score
20	Methyl ethyl ketone (coproduct with acetic acid via n-butane process)	6.4
21	Acetone (coproduct with phenol via cumene hydroperoxide process)	5.6
22	Acrylonitrile (coproduct with hydrogen cyanide)	5.2
	Formic acid (byproduct of acetic acid via n-butane oxidation process)	5.2
24	p-t Butyl benzoic acid	4.8
25	Dimethyl terephthalate (coproduct with terephthalic acid)	4.4
	Acrylic acid	4.4
	Acrolein (byproduct of acrylic acid process)	4.4
28	Isobutyric acid	4.0
29	Styrene (coproduct with propylene oxide via ethylbenzene oxidation process)	3.6
30	Propylene oxide (coproduct with styrene via ethylbenzene oxidation process)	3.2
	a-Methyl styrene (byprduct of acetone via cumene hydroperoxide process)	3.2
	Hydrogen cyanide (coproduct with acrylonitrile)	3.2
33	Propionic acid (propionaldehyde oxidation process)	2.8
	Acetonitrile (byproduct of acrylonitrile process)	2.8
35	Crotonic acid	2.4
36	Cumene hydroperoxide (byproduct of acetone via cumene hydroperoxide process)	2.0

TABLE 9-26 (Continued). CHEMICALS RANKED BY POSSIBLE ECONOMIC EFFECTS OF AO NSPS*

36 AO Chemicals, 29 AO Processes
United States
1978

Rank	Chemical	Score
37	Acetophenone (byproduct of acetone via cumene hydroperoxide process)	1.6
	Cyclohexanol (coproduct with cyclohexanone)	1.6
	Cyclohexanone (coproduct with cyclohexanol)	1.6
40	Ethylene dichloride	-1.2
41	Formaldehyde (silver catalyst process)	-3.4
42	Hydrogen cyanide (Andrussow process)	-11.6

*The larger the possible economic effects are, measured by a combination of the screening criteria results, the higher a chemical-process association appears on the list.

in the analysis. Price increases that might arise from the NSPS are perhaps the most important consideration in this analysis, and all AO chemical industries are examined for price impacts. Therefore, this criterion is weighted most heavily in the ranking scheme. Both profitability and capital availability are assigned values less than the inflation criterion as these tests cannot be performed on all chemical industries; chemical industries that can be considered under the profitability and capital availability criteria are ranked higher simply by their inclusion under these criteria. The reduced weight attempts to counteract this bias. The last criterion, foreign competition, is weighted only if the chemical industry fails the inflation criterion. If a chemical industry experiences no significant price rise, there is no justification for foreign competition impacts.

9.2.8 Individual Chemical Industry Analysis

Individual chemical industries are analyzed further in this section if 1) the chemical industry is not screened out with regard to one or more of the criteria or 2) the chemical industry is found at either of the top three positions on the ranking list. Results of the sensitivity studies are not included in the ranking scheme. As it turns out, most of the chemicals failing a criterion are ranked at the top of the list.

Maleic anhydride (benzene, n-butane) and phthalic anhydride (xylene) are two large volume chemical industries that are not screened out in the first two steps of the price increase analysis; they are examined further in this section to be certain there are no adverse economic effects from pollution control requirements. Worst-case control cost assumptions are relaxed for these two chemicals in order to obtain a more realistic idea of price increase due to the cost of control. Also, the competitive structure of both industries is examined to determine the ability to pass on the incremental control costs if a new facility is built.

Maleic anhydride (benzene) and terephthalic acid are two SOCMI AO chemical industries that are not screened out in the profitability decline analysis; they also are examined further in this section to be certain there are no adverse economic effects from pollution control requirements. The ability to pass through incremental costs is a key element in the individual chemical profitability analysis. The better the ability to pass through incremental process costs, the less harm is done to the firm's profits, assuming quantity demanded does not decrease with the additional price hike. Also, because the standard is imposed only on new sources, the facilities and processes are scrutinized as to the possibility of their being built in the future.

The 1,3-butadiene industry is examined because it is ranked at the top of the list. Special attention is given to capital expenditures because of all the industries examined it is the one that has the highest ratio of capital control investment cost to fixed plant incremental cost.

9.2.8.1 1,3-Butadiene (Capital Constraints). 1,3-butadiene is produced predominantly by recovery from coproduct streams of ethylene-producing steam crackers (80 percent). The remaining 20 percent is produced by air oxidation of n-butane (7 percent) and catalytic dehydrogenation of n-butane (Houdry process, 13 percent). The 1,3-butadiene industry is the number one ranked industry with regard to potential adverse economic effects from the air oxidation NSPS. The industry also has the highest ratio of capital control investment cost to fixed plant incremental cost of all AO industries examined.

Financial information presented in Section 9.1 indicates that AO parent companies should have little difficulty with either debt or equity financing. Table 9-27 lists the 15 firms that produce 1,3-butadiene, their total capital expenditures in 1978, capital expenditures for chemical operations (only for diversified firms if available), and the percentage of company capital expenditures that fall within the scope of normal spending. Copolymer Rubber and Chemical Company has the highest cost of control as a percentage of capital expenditures, almost 25 percent. Copolymer Rubber and Chemical Company is a firm jointly owned by four other companies (see Footnote C, Table 9-27). If these four companies pool their capital, the cost of control, as a percentage of capital expenditures, is reduced by half.

9.2.8.1.1 Supply-side considerations. There are 14 firms producing 1,3-butadiene (see Table 9-28). The majority of capacity is owned by Neches Butane but amounts to only 16.7 percent of the total industry's 1,3-butadiene capacity. Also, Neches Butane has announced plans that it will close its facility. Other immediate future plans include the shutdown of the Phillips facility, an 88 Gg facility to be constructed by El Paso,

TABLE 9-27. CAPITAL CONTROL COSTS AS A PERCENTAGE OF CAPITAL EXPENDITURES BY PRODUCERS
1,3-Butadiene
United States
1978

Firm[a]		Capital expenditures, 1978[b] (1978 $)	Capital cost of control as a percentage of 1978 capital expenditures
Atlantic Richfield Arco Chem. Co. Div.	Total	1,358,000,000	0.6
	Chemicals Only	93,000,000	8.1
Copolymer Rubber and Chemical Corp.	Total	30,782,000[c]	24.5
Dow Chemical	Total	615,000,000	1.2
El Paso Natural Gas	Total	383,000,000	2.0
	Chemicals Only	21,000,000	36.0
Exxon Corporation	Total	4,600,000,000	0.2
	Chemicals Only	246,000,000	13.1
Firestone Rubber & Tire Company	Total	237,000,000	3.3
	Chemicals Only	46,000,000	16.4
Mobil Corporation	Total	1,763,600,000	0.4
Monsanto Company	Total	479,900,000	1.6
Neches Butane Products Company	Total	174,197,000[d]	4.3
	Chemicals Only	64,057,000[d]	11.8
Phillips Petroleum Company	Total	940,200,000	0.8
	Chemicals Only	126,000,000	6.0
Puerto Rico Olefins Company	Total	211,900,000[e]	3.6
Shell Chemical Company	Total	1,774,391,000	0.4
	Chemicals Only	586,000,000	1.3
Standard Oil (Indiana)	Total	2,239,619,000	0.3
	Chemicals Only	228,300,000	3.3
Tenneco Inc.	Total	1,008,000,000	0.7
	Chemicals Only	88,000,000	8.6
Union Carbide Corp.	Total	687,000,000	1.1

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[a] SRI International. 1978 Directory of Chemical Producers, United States of America.

[b] Securities and Exchange Commission - 10 K Reports. Washington, D.C.

[c] Copolymer and Chemical Corporation is 40 percent owned by Armstrong Rubber, 20 percent owned by Gates Rubber Company, 20 percent owned by Mansfield Tire and Rubber Company, and 20 percent owned by Sears Roebuck and Company.

[d] Neches Butane Productions Co. is owned jointly by BF Goodrich Chemical Co. and Texas-U.S. Chemical Company.

[e] Puerto Rico Olefins Company is owned jointly by Commonwealth Oil Refining Company, Inc. and PPG Industries, Inc.

TABLE 9-28. 1,3-BUTADIENE CAPACITY, BY PRODUCER
United States
1978

Firm	Annual capacity (Gg)	Percentage of total capacity
Amoco	72	3.8
Arco	240	12.5
Copolymer	64	3.3
Dow	34	1.8
El Paso	80	4.2
Exxon	228	11.9
Firestone	96	5.0
Mobil	20	1.0
Monsanto	40	2.1
Neches Butane	320	16.7
Petro-Tex	300	15.7
Phillips	124	6.5
Shell	200	10.4
Union Carbide	98	5.1
TOTAL	1916	100.0

SOURCE: SRI International. 1978 Directory of Chemical Producers, United States of America.

and a 200 Gg facility to be built by Shell. The net result in terms of market concentration is that Shell will own the most 1,3-butadiene capacity, equalling 23 percent of the total capacity.

With the relatively large number of firms producing 1,3-butadiene and capacity spread fairly equally among four or five firms, the industry can be termed price-competitive. An additional 1,3-butadiene facility is expected to be built from 1981 through 1986. Even if Shell should build this new facility (which is doubtful given that they are just completing one), Shell would still not possess the market power to dictate prices. The domestic 1,3-butadiene industry also faces significant competition from foreign imports (17 percent of domestic 1,3-butadiene consumption is imported), making it difficult for one firm to set higher prices.

A tight supply condition in the future may be conducive to the industry's ability to raise 1,3-butadiene price. The supply condition would evolve from raw material economics. Most 1,3-butadiene facilities are dependent on coproduct extraction from ethylene-producing steam crackers and are built to use naphtha or gas oil as the major raw material. Because light hydrocarbons such as ethane, propane, and butane are less expensive than naphtha and gas oil, raw material substitution is presently occurring. The result of using the lighter hydrocarbons is that the 1,3-butadiene content of feed streams from ethylene units will drop.

9.2.8.1.2 Demand-side considerations. The major end use of 1,3-butadiene is related primarily to the automotive industry. Forty-five percent of the 1,3-butadiene produced is used to make styrene-butadiene rubber (SBR) which goes into tires. Unfortunately for 1,3-butadiene producers, the tire business has been a leading casualty of the energy crisis. Smaller cars, radial tires, and a general decline in automobile production have hurt the tire industry. A significant resurgence of demand in this area seems unlikely. Demand for SBR will decline or, at best, remain flat. Output of other types of rubber such as polybutadiene rubber and neoprene that need 1,3-butadiene may not decline, but neither will they grow very much in the near future. The one bright spot for 1,3-butadiene use is acrylonitrile-butadiene-styrene (ABS). Growth in demand for ABS is projected to be 5 to 7 percent annually, but because ABS consumes only 6 percent of 1,3-butadiene production, ABS will be of little help in increasing the overall 1,3-butadiene demand.

The price of 1,3-butadiene certainly will not increase due to demand pressures. Prices will rise as raw material costs increase. Producers may have a difficult time totally passing through pollution control costs because of poor demand conditions. As a result, profitability decline due to pollution control costs will be minor when compared to the profitability repercussions caused by a flat demand situation.

9.2.8.2 Maleic Anhydride (Price Increase and Profitability Decline). Maleic anhydride is made using an AO process and either benzene or n-butane as the main feedstock. The chemical shows a price increase due to the incremental costs of control greater than 5 percent when these control costs are tabulated initially. When the worst-case control cost assumptions are relaxed, maleic anhydride made from benzene experiences a price rise of 4.2 percent and maleic anhydride produced using n-butane shows a price increase of 3.1 percent.

Also, the maleic anhydride (via benzene) facility is found to have unfavorable profitability when pollution costs are added, while the maleic anhydride (via n-butane) facility experienced no such adverse effect. The failure of benzene-feedstock maleic anhydride under the profitability criterion may be discounted because it is likely that any new maleic anhydride sources will use n-butane as their only feedstock. Monsanto's new facility will use n-butane, and it is presently planning to convert its St. Louis plant to n-butane feedstock. Ashland and Denka will change over to an n-butane feed and Koppers is considering replacing its benzene feedstock facility with one using n-butane.[72]

n-Butane appears to have some clear economic advantages over benzene as a feedstock. There are two important reasons why the n-butane process is more profitable than the benzene process and why new maleic anhydride facilities will more than likely use an n-butane feed. First, the cost of n-butane is substantially less than the cost of benzene. Contract n-butane currently sells for about 20 cents per kilogram while benzene costs approximately 46 cents per kilogram. The difference is tempered somewhat by the fact that a kilogram of benzene yields slightly more maleic anhydride than a kilogram of n-butane and that the price of n-butane increases by approximately 40 percent during the winter months; however, unlike other petrochemical feedstocks, the price of n-butane may decrease in the future as supply increases. The second reason is availability: market forecasts indicate large surpluses of n-butane for the 1980's.[73] n-Butane also comes from two sources, oil and natural gas, providing better insurance against supply interruptions.

9.2.8.2.1 Supply-side considerations. The maleic anhydride industry is very competitive. Market shares are not concentrated; no one firm owns more than 21 percent of the total capacity (see Table 9-29). The major areas of competitive pricing involve the merchant market rather than the captive market. Merchant sales comprised 75 percent of the maleic anhydride consumed in 1977 with captive consumption at 20 percent and imports at 5 percent. While cost may be passed through both the merchant and captive markets, the greatest effect is seen in the highly competitive merchant market.

The captive market price increments emerge in the final product, having been diluted by costs of other constituents also necessary to produce the final product. The effect of this "dilution" is substantial: for example, approximately 15 percent of the wholesale price of unsaturated polyester resins is attributed to maleic anhydride.

On the supply side, it appears that the incremental cost of pollution controls would not raise the price of maleic anhydride substantially, if at all, because the industry is competitive in its pricing practices. Monsanto is slated to build a new facility with a capacity of 60 gigagrams in the first quarter of 1981. (If started on schedule, the Monsanto plant would not be affected by the NSPS.) Monsanto, with this new facility, would own almost 50 percent of total maleic anhydride capacity. Monsanto then could become the industry price leader. However, it has been estimated that the amount of maximum additional maleic anhydride capacity that will be built from 1981 through 1986 is 138 gigagrams. This additional capacity, if built by one or more different firms, would dilute Monsanto's market advantage and no firm would have the market power to raise price based on its incremental control costs alone.

9.2.8.2.2 Demand-side considerations. While there appears to be fairly intense competition among manufacturers of maleic anhydride, little import competition exists. Also, the competition from similar products that may serve as substitutes is not great. This situation usually results

TABLE 9-29. MALEIC ANHYDRIDE CAPACITY, BY PRODUCER
United States
1978

Firm	Annual capacity (Gg)	Percentage of total capacity
Ashland Oil	27.2	11.6
Denka Chemical	22.7	9.7
Koppers	20.0	8.6
Monsanto Company	47.6	20.4
Reichold Chemicals	40.8	17.5
Standard Oil Company of Indiana	27.2	11.6
Tenneco	11.8	5.1
United States Steel	36.3	15.5
TOTAL	233.6	100.0

SOURCE: SRI International. 1978 Directory of Chemical Producers, United States of America.

in an incremental cost pass-through ability in times of high demand for the product and the inability to pass through all or part of an additional cost increase during periods of low demand.

Substitutes may exist for maleic anhydride itself as well as for the products that use maleic anhydride as an input material, depending on the end use. The predominant end use of maleic anhydride is in the production of unsaturated polyester resins. Of the 151 gigagrams of maleic anhydride produced in 1978, polyester resins consumed 54 percent or 82 gigagrams. Polyester resins go into reinforced plastic applications such as marinecraft, building panels, automobiles, tanks, and pipes. Maleic anhydride, unlike most of the other input materials used to make unsaturated polyester, is a necessary input because it is the source of unsaturation and is necessary to cross-link the polyester with the reactive dilutent.

The agricultural chemicals market is the second largest market for maleic anhydride (10 percent of total demand). Although other chemicals can substitute for maleic anhydride as an agricultural chemical, it is highly competitive in this market. Unsaturated polyester resins and agricultural chemicals have the potential to be high growth products in the future and may provide the necessary demand conditions to pass through fully any pollution control costs. Other markets, such as lubricants, maleic anhydride copolymers, fumaric acid, and reactive plasticizers, are mostly mature with little possibility of additional market penetration by maleic anhydride.

The maleic anhydride industry has indicated that it would not raise prices under low demand market conditions but rather, because manufacturers of maleic anhydride are a small part of large parent firms, would pass through pollution control costs partially or totally to other products.[74] Recently, sellers, buyers, and dealers of maleic anhydride have agreed that pricing for the product has been extremely weak because capacity utilization has been low, approximately 10 percentage points below the industry average.

In addition, the presently weak pricing situation is predicted to continue. Unsaturated polyester resins seem to be a guiding factor and are heavily dependent on construction and automotive needs, two areas that may continue to stall. As a result of the inability to pass through the cost increase, the impact of the standard will be greater on profitability than on inflation.

9.2.8.3 Phthalic Anhydride (Price Increase). Phthalic anhydride is produced using an AO process and either xylene or naphthalene as the main feedstock. Phthalic anhydride using xylene initially has a price increase of greater than 5 percent; after the worst-case control costs are modified, its 1986 price impact decreases to 3.5 percent when xylene is the feedstock and 2.2 percent when naphthalene is the feedstock. The two feedstock materials are fiercely competitive; approximately 50 percent of phthalic anhydride is produced from xylene and 50 percent from naphthalene. The similar percentage price increases point out that possible competitive disadvantages for either feedstock can be discounted when pollution control requirements are imposed on new phthalic anhydride facilities.

The phthalic anhydride industry is similar to the maleic anhydride industry in terms of market competition. Phthalic anhydride has a large merchant market (60 percent of the phthalic anhydride sold), little competition from imports, few substitutes for the product itself or its end uses, and a highly competitive intra-industry atmosphere.

9.2.8.3.1 Supply-side considerations. There are nine chemical firms producing phthalic anhydride, none of which owns more than 26 percent of the total capacity (See Table 9-30). Recently, Exxon raised its capacity from 59 to 95 gigagrams in the fourth quarter of 1980.[75] Also, United States Steel and Tenneco Chemicals, in a joint effort, broke ground early in 1981 on a 95-gigagram xylene-based phthalic anhydride operation. These two facilities will not be affected by the AO NSPS because they will be started before the standard is proposed. The addition of this capacity will not change the competitive nature of the phthalic anhydride industry. United States Steel would own the most capacity -- also 26 percent of the total capacity. Additional phthalic anhydride capacity to be built and replaced from 1981 through 1986 is projected to be 165 gigagrams (three projected plants multiplied by an average capacity of 55 gigagrams each). If an existing company with a substantial stake in the phthalic market (such as Koppers or United States Steel) builds a new facility and gains a greater market share, then, in the role of price leader, it may be able to pass on the incremental costs of control. Again, this would be possible

TABLE 9-30. PHTHALIC ANHYDRIDE CAPACITY, BY PRODUCER
United States
1978

Firm	Annual capacity (Gg)	Percentage of total capacity
Allied Chemical	18.1	3.0
BASF Wyandotte	68.0	11.3
Exxon	59.0	9.8
Koppers	152.0	25.3
Monsanto	99.8	16.5
Occidental Petroleum	45.4	7.5
Standard Oil Company of California	22.6	3.7
Stephan Chemical	45.4	7.5
United States Steel	93.0	15.4
TOTAL	603.3	100.0

SOURCE: SRI International. 1978 Directory of Chemical Producers, United States of America.

only if the general economy and overall demand are healthy so that the automobile and housing sectors have a few strong years.

9.2.8.3.2 Demand-side considerations. Fifty percent of the phthalic anhydride produced is used in phthalate plasticizers, 24 percent in unsaturated polyester resins, 19 percent in alkyd resins, and the remaining 7 percent in miscellaneous uses. The main use of phthalate plasticizers is in polyvinylchloride. The phthalic anhydride used to produce unsaturated polyester resins is not a substitute for maleic anhydride, but rather a complementary input.

Two phthalic acids -- terephthalic and isophthalic -- are substitutes for phthalic anhydride but usually will not compete because of their higher process costs. There are a few cases of resin use in which the higher prices of terephthalic and isophthalic acids might be justified.

The end uses of phthalic anhydride are related predominantly to the automotive and housing markets. Thus, the ability to increase prices depends mainly on the general level of the economy. In a time of recession, phthalic anhydride producers find it difficult to increase price. Phthalic anhydride does have one outlet (alkyd resins) that is not dependent on the state of the economy. Phthalic anhydride, polyhydric alcohol, and fatty oils combine to produce alkyd resins that serve as the bases of various industrial paints. Sales of alkyd resins have remained constant through the current recession.

Overall, because of an indifferent market and competitive pressures, the price of phthalic anhydride currently has been termed "weak" and profitability has suffered. Phthalic producers have had trouble passing through the rising costs of xylene. This inability to raise price originates from the competitive pressure of naphthalene-based producers and from slow automotive sales and below-normal housing starts.

9.2.8.4 Terephthalic Acid (Profitability Decline). Almost the entire amount of terephthalic acid (TPA) consumed is used in the production of polyethylene terephthalate, the polymer used in the manufacture of polyester fibers and polyester films. Polyester fibers account for 91 percent of the polyethylene terephthalate consumed; polyester films, for 7 percent. TPA can be substituted easily by dimethyl terephthalate (DMT) in the production of polyethylene terephthalate; DMT is produced as a coproduct with TPA and would have similar control costs imposed upon it.

TPA has been experiencing a greater growth in production than has DMT for two reasons. First, at equal prices, TPA has a cost advantage over DMT on the basis of material requirement per pound of polymer manufactured (about 14 percent less TPA is needed than DMT). Second, somewhat shorter reaction times are required if TPA is used, although DMT-based processes are more economical for batch operations (important when a large number of different fiber grades are being produced) and for the production of fibers with more consistent dyeing properties. It appears that TPA producers should not have a problem passing through control costs from fear of substitutes because DMT also experiences the incremental cost of control and, in general, because TPA has process economic advantages over DMT. In addition, there is little chance of a non-AO process being substituted to produce TPA, because a more economical one does not yet exist.

Intra-industry competition does not appear to be very intense. There are only two firms producing TPA: Standard Oil Company-Indiana (Amoco Chemicals Corporation) owns 88 percent of the total capacity and Hercofina owns the remainder. It appears that these two firms are able to boost their prices when costs increase. Recently, the price of the basic raw material, p-xylene, rose dramatically, pressured by demand for mixed xylenes in gasoline. The two TPA producers were able to increase the price of their monomer equivalently. In turn, there has been pressure on polyester prices to increase even though, traditionally, the textile industry has strongly resisted price increases.

The primary substitute for polyesters is cotton. The historically strong growth rate for TPA -- 16 percent per year, 1968-1978 -- has been due to the replacement of cotton by polyesters in the textile industry. However, if polyester fiber prices increase, cotton might retrieve some of its lost market share.

With a strong growth rate projected (7.5 percent annually), and the apparent ability to pass on increased costs of production, the profitability of the TPA process should face no significant setbacks due to pollution control.

9.3 POTENTIAL SOCIOECONOMIC AND INFLATIONARY IMPACTS

If all new SOCMI sources that use an air oxidation process are required to purchase and operate an incinerator, the socioeconomic impacts can be summarized as follows:

Annualized Costs. Annualized costs in the fifth year following proposal are expected to be $67 million (1978 $) if all 49 projected new AO sources are controlled. The annualized control costs are before-tax, projecting the total dollar costs of control not just to industry, but to society as a whole. The 49 projected new sources represent facilities to be constructed because of additional growth in demand as well as new facilities needed to replace obsolete existing capacity.

Price Impacts (Inflation). All of the 36 chemicals produced using the AO process have price increases of less than 5 percent. Because all of the chemicals are intermediates, downstream products will have even smaller price increases due to the NSPS. The effect on the consumer price index appears negligible.

Employment Impacts. Adverse impacts on employment can be discounted because an NSPS on AO processes has no affect on current demand. The amount of labor required to operate a thermal incinerator is estimated to be one person. Therefore, with 49 new facilities projected to be built, 49 workers would be hired as a result of the imposition of an NSPS on SOCMI.

Distributional Impacts. The standard is worded such that some new facilities will be exempt from installing control equipment because they will be above a defined total resource effectiveness (TRE) floor (see Chapter 6). New facilities that fall below the floor would be required to make a pollution control expenditure. A national profile of AO facilities as defined in Chapter 6 has 11 of 59 existing facilities falling below the TRE floor when regulatory alternative III is examined. Regulatory alternative III represents an estimate of the most practical approach for implementing the standard. The 11 facilities are examples from a current sample. It is impossible to predict that new facilities complying with the standard will be similar to the 11 facilities from the national profile. In any case, the 11 existing facilities are used to examine whether the standard causes disproportionate burdens on various segments such as specific chemical industries, specific companies, geographical areas, small versus large facilities, and end use types.

Of the 11 facilities that fall below the TRE floor, 4 produce acrylonitrile, 3 produce ethylene oxide, 2 produce ethylene dichloride, 1 produces cyclohexanol/cyclohexanone, and 1 produces maleic anhydride. The acrylonitrile industry not only has the largest number of facilities being controlled in absolute terms, but also has the highest percentage of existing facilities using an air oxidation process being controlled -- 4 of 5 existing acrylonitrile facilities fall below the TRE floor.

The 11 facilities are owned by 10 separate firms. Only Dow owns more than one of the facilities that requires additional pollution control expenditures. Hence, the distributional burden of the standard is shared almost equally among firms that must comply with regulatory alternative III. Also, all firms that own the 11 facilities below the TRE floor are large, diversified, and financially strong entities. The small, marginal companies are not affected.

Eight of the 11 facilities are located in Texas and Louisiana. Only 40 percent of all facilities that produce air oxidation chemicals are located in Texas and Louisiana. Facilities affected appear to be larger in capacity than the norm. The size of the 11 facilities ranges from a capacity of 14 gigagrams to a capacity of 726 gigagrams. The average capacity is 153.6 gigagrams and this compares to an average capacity of 119.1 gigagrams for all facilities producing air oxidation chemicals. Finally, all of the chemicals falling below the TRE floor are used in the production of polymers and resins.

Regulatory Flexibility Act Considerations. The Regulatory Flexibility Act (RFA) became effective on January 1, 1981, and requires agencies to consider flexible regulatory approaches that minimize the economic impact of regulations on small entities. Specifically, the RFA states that a thorough impact analysis be undertaken if the proposed standard has a significant economic impact on a substantial number of small entities. Entities such as not-for-profit organizations and small governmental jurisdictions do not experience any perceivable effects from the SOCMI AO NSPS. Only small businesses are affected by the AO standard. To determine if the AO NSPS merits a detailed analysis, a small business for the AO industry must be defined.

Under Section 121-3-1b of the Small Business Administration Rules and Regulations, a small business concern is defined by an employment size standard for each four-digit Standard Industrial Classification (SIC) code. This is the measure used to determine a small business concern for the purpose of pollution control guarantee assistance. Also, a business is considered small only if it is owned and operated independently. AO chemicals are included in SIC 2865 and SIC 2869 and their size standards are 750 and 1,000 employees, respectively. The definition of a small business for SIC 2865 is applied to all AO chemical manufacturers because it is more conservative.

There are 75 companies that produce AO chemicals (listed in Table 9-4). More than half of the companies using the AO process are ranked in the top 50 chemical-producing companies based on value of chemical sales in 1979.[76] A survey of the number of employees per company from Standard and Poor's Register of Corporations, Directors and Executives, 1981 reveals that only three companies, Kalama Chemicals, Inc., Wright Chemical Company, and Copolymer Rubber and Chemical Corporation, have fewer than 1,000 employees and qualify as small businesses. Therefore, less than 3 percent of the affected companies are small businesses. A brief discussion of the effect of the NSPS on small businesses follows.

Since this standard applies primarily to new sources, it is difficult to estimate its specific adverse effect on projects that will be undertaken by small businesses entering the industry. In general, if a company has the capital available to enter the industry, the NSPS will require only a small percentage increase in the capital required for the project. Furthermore, the price impact screening results suggest that producers of AO chemicals, under a worst-case scenario, are able to pass through NSPS compliance costs to their customers while keeping the price increase of their product under 5 percent. Most importantly, however, the economies of scale that exist in this industry hinder the entrance of small businesses. Therefore, even without the NSPS, the AO industry is not conducive to small businesses. In the five years following proposal of the NSPS, small businesses should not constitute a greater share of AO producers than they currently do, i.e., 3 percent of AO firms.

Costs and Benefits. Executive Order 12291 specifies that a regulatory action, to the extent permitted by law, must not be undertaken unless the potential benefits to society from the regulation outweigh the potential costs to society. An exhaustive benefit-cost analysis is not appropriate here because the potential air oxidation emissions standards will not constitute a major rule within the meaning of the Executive Order because the cost of the standards and their overall impact on the economy are not expected to be significant.

The costs of the potential standard are not exorbitant, especially when the significant benefits that will accrue due to the standards are examined. Estimated net annualized costs for the most stringent standard as well as the regulatory alternative most apt to be chosen are small in comparison with industry output. The cost analysis focused on the potential costs of the standards, and the impact of these costs on producers of SOCMI chemicals. Based on these costs and the impacts of the costs, the costs of the standards are considered feasible. The benefits of the standards, as discussed below, may be compared subjectively with the costs.

Because environmental quality is a public good, it is necessary to use an indirect approach to valuing the changes in environmental quality. These approaches generally use market data and attempt by regression analysis to infer values for improvements in air quality from individuals' behavior or to solicit such values by directly questioning the affected individuals. EPA is at the forefront of benefits estimation, both in the knowledge of various methodologies and in the practical application of these methodologies to various standards given data constraints. These benefit analyses involve a substantial investment of time and resources and they have limitations. EPA does not think that a full benefits analysis is warranted for the potential air oxidation emissions standards, given that the net costs that EPA has estimated for the most stringent standard are relatively small and the expected improvements in environmental quality are significant.

These standards will reduce the rate of VOC emission to the atmosphere. VOC are precursors of photochemical oxidants, particularly ozone. The EPA publication, Air Quality Criteria for Ozone and Other Photochemical Oxidants (EPA-600/8-78-004, April 1978), explains the effects of exposure to elevated ambient concentrations of oxidants. (The problem of ozone depletion of the upper atmosphere and its relation to this standard are not addressed here.) These effects include:

- Human health effects - ozone exposure has been shown to cause increased rates of respiratory symptoms such as coughing, wheezing, sneezing, and short-breath; increased rates of headache, eye-irritation, and throat irritation; and increases in the number of red blood cells (changes in erythrocytes). One experiment links ozone exposure to human cell damages known as chromosomal aberrations.

- Vegetation effects - reduced crop yields as a result of damages to leaves and/or plants have been shown for several crops including citrus, grapes, and cotton. The reduction in crop yields was shown to be linked to the level and duration of ozone exposure.
- Materials effects - ozone exposure has been shown to accelerate the deterioration of organic materials such as plastics and rubber (elastomers), textile dyes, fibers, and certain paints and coatings.
- Ecosystem effects - continued ozone exposure has been shown to be linked to structural changes of forests such as the disappearance of certain tree species (Ponderosa and Jeffrey pines) and death of predominant vegetation. Hence, continued ozone exposure causes stress to the ecosystem.

In addition to the evidence of the physical and biological effects enumerated above, reduction of VOC emissions is likely to improve the aesthetic and economic value of the environment through: 1) beautification of natural forests and undeveloped land through increased vegetation; 2) increased visibility; 3) reduced incidence of noxious odors; 4) increased life for works of art, including paintings, sculpture, architecturally important buildings, and historic monuments; 5) improved appearance of structures, sculptures, and paintings, and 6) improved productivity of workers, especially farm laborers.

Also, the potential air oxidation NSPS provides other direct public goods to society including: 1) improvement of business decision making; 2) optimization of industrial location; and 3) acceleration of technological innovation. The nature of each of these benefits is discussed below:

- Decision making - the collection of data, evaluation of control technologies on specific processes, and the publication of this information in the form of control technique guidelines, background information documents, and other reports represent benefits to many businesses (in particular small businesses) that do not have the resources to implement such an exhaustive information processing system.
- Industrial location - a nationwide standard of performance for VOC emissions is likely to remove the incentives for possibly suboptimal plant locations in states with relatively weak State Implementation Plan (SIP) emissions standards, as opposed to states with relatively stringent SIP emissions standards.

- Technological innovation - the information generated through the regulatory process may accelerate the development of new technologies by businesses.

FOOTNOTES

1. The value of shipments for SIC 28 in 1978 is $130,000,000,000 and for SIC 286 is $31,800,000,000 (from U.S. Department of Commerce. 1979 U.S. Industrial Outlook). The AO chemicals' value of shipments was found using Tables 9-1 and 9-2. Production was multiplied by percentage sold and this was multiplied by market price for each particular chemical. The products were summed to give a value of shipments for the chemicals listed in Table 9-2. This amount was extrapolated based on capacity to include all 36 chemicals. The value of shipments for all air oxidation chemicals is estimated to be $3,188,100,000 for 1978.

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APPENDIX A TO CHAPTER 9

APPENDIX A
NET PRESENT VALUE FORMULA

The formula for net present value (NPV) is designed to measure the cash flows that account for the profitability of investments in new facilities to manufacture synthetic organic chemicals. Table A-1 presents the formula in equation form. The formula is complex but is based on simple concepts. The NPV formula reflects the sum of cash outflows and inflows, discounted each year to their equivalent values in the base year. A discount factor, $(1+D)^{-i}$, appears often in the formula. This reflects the fact that cash flows in future years (i) are worth less than current cash flows with the same nominal value. D is the hurdle rate that new projects must meet to overcome this time value difference and be competitive with other potential uses of firms' capital. Cash outflows are: investments in fixed facilities and equipment, F, and incinerators for emissions control, X; additions to working capital (the excess of total investment, T, over fixed investment, F); annual operating costs; and taxes on profits. Cash inflows are: revenues on production sold each year (price, P, times quantity, Q); and receipts after taxes from liquidation of working capital at the end of the equipment's useful life.

There are some complexities in the formula and some simplifications. One area of complexity reflects the fact that costs and prices are inflating each year. A factor is used for general price inflation, G, and in some cases an additional factor for real escalation, R, for items that are oil-based. Because organic chemicals are petrochemical derivatives, they escalate in cost at rates in excess of the inflation rate for consumer goods in general. At the same time, some items do not inflate at all. Depreciation allowances do not change with inflation, necessitating special treatment in formula terms.

TABLE A-1. NET PRESENT VALUE FORMULA

Line 1 $NPV = -(1+D)^{-0.5}(1+G)^{0.5}F$

Line 2 $-(1+D)^{-0.5}(1+G)^{0.5}X$

Line 3 $-(1+D)^{-1}(1+R)(1+G)(T-F)$

Line 4 $+\sum_{i=1}^{20}(1+D)^{-(i+0.5)}\{0.5[(1+R)^{i+0.5}(1+G)^{i+0.5}$

$(P\cdot Q-C-Y)]+0.05F\}$

Line 5 $-(1+D)^{-10.5}(1+G)^{10.5}X$

Line 6 $+\sum_{i=1}^{10}0.1(1+D)^{-(i+0.5)}X+\sum_{i=11}^{20}0.1(1+D)^{-(i+0.5)}(1+G)^{10.5}X$

Line 7 $+(1+D)^{-21}\,0.5[(1+R)^{21}(1+G)^{21}+(1+R)(1+G)](T-F)$

where:

F = Fixed investment in facilities (does not include incinerator costs)
T = Total investment (does not include incinerator costs)
D = Hurdle rate used in discount factor
R = Rate of real escalation in prices
G = Rate of general price inflation
P = Price of chemicals
Q = Production quantity
C = Cost of production, excluding costs for emission controls
X = Investment costs for incinerator
Y = Incinerator operating costs
i = Year

Note: Figures are in 1978 dollars.

Lines 1 and 2 of the equation in Table A-1 show investments in equipment. Fixed investment in the facility and equipment is shown as F. Purchase of the first incinerator for emission control is shown as X. Each cash flow takes place at a certain point or period along a time line. Investment in the basic facilities and equipment is assumed to take place over the course of year 0. It is therefore allocated as a lump sum to the middle of year 0 and is adjusted accordingly with one half year's inflation and discounted at one half year's discount rate. The incinerator is assumed to be purchased at mid-year in year 0 also. Hence, the first two terms, respectively, are $(1 + D)^{-0.5}(1 + G)^{0.5}F$ and $(1 + D)^{-0.5}(1+G)^{0.5}X$. (A negative exponent denotes "the reciprocal of" while a fractional exponent denotes a fraction of one year.)

Line 3 shows the initial working capital investment. Working capital (mainly product inventory) is the excess of total investment, T, over fixed investment, F. Working capital is produced and stored at the beginning of year 1, so the cash flows must reflect some inflation and must be discounted by one year's discount factor. Unlike the investments mentioned above, working capital also escalates in value by a real escalation factor that reflects the above-average rate of increase assumed for oil derivatives. Hence, an extra term, 1 + R, where R is the rate of real escalation for oil and petrochemical prices, is applied in a compound fashion. Line 3 is therefore $(1 + D)^{-1}(1 + R)(1 + G)(T - F)$.

Line 4 is complex and will be explained later. Moving ahead in the formula, line 5 shows the purchase of a second incinerator. Unlike general facilties and equipment, which are assumed to last for 20 years of production, incinerators are assumed to last 10 years. A second incinerator is purchased at mid-year in year 10 to be used at the beginning of year 11 and last through the end of year 20. The outlay for the second incinerator is $(1 + D)^{-10.5}(1 + G)^{10.5}X$.

Line 6 will also be explained later. Line 7 shows the recovery of working capital when product inventory, accumulated earlier in year 1, is sold off as the facility finishes operations at the outset of year 21. The value of inventory will have risen with inflation in general, G, and with real escalation in the value of oil-based chemicals, R. The appreciation in value over 20 years will produce profits that are taxable, such that 50 percent of the increase will be deducted for taxes. The whole expression for the liquidation of working capital is $(1 + D)^{-21} 0.5\ [(1 + R)^{21} (1 + G)^{21} + (1 + R)(1 + G)]\ (T-F)$. The figures in brackets represent the increase in the value of working capital, $T - F$.

Returning to line 4, the cash flows involved in production and sales are depicted. Essentially, for each year from 1 through 20, a project will earn revenues (price, P, times production quantity, Q) and pay costs (production costs, C, and control costs, Y, reflecting operating costs of incinerators). The term $(P \cdot Q - C - Y)$ indicates accounting profits, which are taxable at a 50 percent rate. Inflation is reflected in the terms $(1 + R)^{i+0.5}(1 + G)^{i+0.5}$ used as coefficients. Half years were used because costs and revenues are annual streams, such that their weighted averages lie roughly at the mid-year points in each year. The term i refers to each year from 1 through 20.

Depreciation is an unusual cost item. It is actually a cost allowance for an annual share of investments made in previous years, not a cash flow. There is no cash flow for depreciation, but depreciation charges reduce accounting profits and, therefore, reduce firms' taxable incomes and tax payments (which are cash flows). To correct for the inclusion of depreciation in production costs, C, depreciation is added back as the term 0.05 F. The depreciation term reflects straight-line depreciation of the fixed investments over 20 years.

Line 6 presents the depreciation on the incinerators. The first incinerator is depreciated from year 1 through 10. The second incinerator is depreciated from year 11 through 20. Because incinerators last 10 years, a factor of 0.1 is applied to investment costs, X. The investment cost for the second incinerator reflects inflation over 10.5 years and hence is multiplied by $(1 + G)^{10.5}$. Both expressions for depreciation include a discount factor $(1 + D)^{-(i+0.5)}$.

Not shown in the formula is the assumption that the facility shutdown costs equal scrap value in year 20. These net out to zero and, therefore, need not be shown. Land costs, which are not included in fixed investment, also are assumed to be a neutral factor over the life of a project; resale value is assumed to allow the original investment to be recouped with an appropriate return to cover the discount factor.

Other simplifications have been made. Depreciation is calculated on a straight-line basis. Actual depreciation rates would be more accelerated, so the use of straight-line accounting understates NPV slightly. Another simplification is the use of variables as entities even though each cost or revenue item involves subcomponents whose behavior over 20 years may vary from the average. Finally, the timing of cash flows is necessarily approximate. The goal in constructing a time line is to approximate the timing of major cash flows so that the proper inflation and discount factors can be applied.

The baseline NPV is calculated by setting incinerator investments, X, and the incinerator operating costs, Y, equal to zero. When emissions standards must be met, proper values for X and Y are applied with the assumption that there is no pass-through of control costs in the price of the chemicals.

APPENDIX A: EVOLUTION OF THE PROPOSED STANDARDS

APPENDIX A
EVOLUTION OF THE PROPOSED STANDARDS

The purpose of this study was to develop New Source Performance Standards for Air Oxidation Unit Processes of the Synthetic Organic Chemical Industry (SOCMI). Work on the study was begun in March 1979 by Energy and Environmental Analysis, Inc. under the direction of the Office of Air Quality Planning and Standards (OAQPS), Emission Standards and Engineering Division (ESED). The decision to develop this standard was made on the recommendation of Hydroscience (now I.T. Enviroscience, Inc.) based upon information compiled under their contract to develop a technical data base for NSPS's for SOCMI. In performing the standard development, EEA used product reports and background technical documents prepared by Hydroscience.

The chronology which follows lists the important events which have occurred in the development of background information for the New Source Performance Standards for air oxidation unit processes of SOCMI.

Date	Activity
May, 1979	Statistical analysis of air oxidation industry and process emissions initiated.
August, 1979	Draft industry wide statistical profile submitted to EPA by EEA.
August, 1979	Cost analysis submitted to EPA by EEA.
October 25, 1979	Meeting with CMA, EAB, SDB, CPB, and EEA to introduce CMA to the generic approach and method of analysis.
January 9, 1980	Meeting with CMA, EPA and EEA to bring industry up to date on the proposed method of analysis and to elicit industry comments.
February 6, 1980	Meeting with CMA, EPA, and EEA to discuss progress of unit process standard.
March 30, 1980	Meeting with CMA, EPA, and EEA to brief CMA on the status of SOCMI projects.
May 5 and 6, 1980	Meeting with CMA, EPA, and EEA to brief CMA on the flow predictor analysis, national impact analysis, and affordability screening criteria.
August 18, 1980	Meeting with CMA, EPA, and EEA to discuss issues raised on EEA analysis of affordability screening.
August 19, 1980	Meeting with CMA, EPA, and EEA to brief CMA on the status of the project.
January, 1981	BID Chapters 3-6 sent out for review by industry and environmental groups.
January, 1981	Final revised affordability screening, national impact, and sensitivity analyses provided to EAB contractor.
April 30, 1981	Meeting with CMA to discuss their final report on Air Oxidation Regulatory Development.
June 30, 1981	Working group package mailed.
July 6, 1981	Meeting with CMA to discuss Working Group Package.
August 8, 1981	Package transmitted to NAPCTAC/Steering Committee.
August 18, 1981	Docket transmitted to Washington, D.C.
September 23, 1981	NAPCTAC Meeting.

APPENDIX B: INDEX TO ENVIRONMENTAL CONSIDERATIONS

APPENDIX B

INDEX TO ENVIRONMENTAL CONSIDERATIONS

This appendix consists of a reference system which is cross indexed with the October 21, 1974 Federal Register (39 FR37419) containing EPA guidelines for the preparation of Environmental Impact Statements. This index can be used to identify sections of the document which contain data and information germane to any portion of the Federal Register guidelines.

APPENDIX B

INDEX TO ENVIRONMENTAL IMPACT CONSIDERATIONS

Agency Guidelines for Preparing Regulatory Action Environmental Impact Statements (39 FR 37419)	Location Within the Background Information Document (BID)
1. Background and Description of proposed Action	
Summary of Regulatory Alternatives	The regulatory alternatives are summarized in Chapter 1, Section 1.1.
Statutory basis for the Standard	The statutory basis for the standard is given in Chapter 1, Section 1.1.
Facilities Affected	A description of the facilities to be affected is given in Chapter 6.
Process Affected	A description of the processes to be affected is given in Chapter 3, Section 3.3.
Availability of Control Technology	Information on the availability of control technology is given in Chapter 4.
Existing Regulations at State or Local Level	A dscussion of existing regulations on the industry to be affected by the standards is included in Chapter 3, Section 3.5.
2. Alternatives to the Proposed Action	
Alternatives 0, I, II, III, IV, V, and VI	
Definition of alternatives	The definitions of alternatives 0, I, II, III, IV, V, and VI are presented in Chapter 6, Section 6.2.

APPENDIX B

INDEX TO ENVIRONMENTAL IMPACT CONSIDERATIONS
(CONTINUED)

Agency Guidelines for Preparing Regulatory Action Environmental Impact Statements (39 FR 37419)	Location Within the Background Information Document (BID)
Environmental Impacts	
Air Pollution	The air pollution impact of the control alternatives are considered in Chapter 7, Section 7.1.
Water Pollution	The impact of the control alternatives on water pollution are considered in Chapter 7, Section 7.2.
Solid Waste Disposal	The impact of the control alternatives on solid waste disposal are considered in Chapter 7, Section 7.3.
Energy	The impact of the control alternatives on energy use are considered in Chapter 7, Section 7.4.
Other Impacts	Other impacts associated with the control alternatives are evaluated in Chapter 7, Sections 7.5 and 7.6.
Costs	The impact of the control alternatives on costs are considered in Chapter 8, Section 8.1.

APPENDIX C: EMISSION SOURCE TEST DATA

APPENDIX C: EMISSION SOURCE TEST DATA

The purpose of this appendix is to describe results of tests of volatile organic compound (VOC) emissions reduction by thermal incineration. These test results were used in the development of the background information document (BID) for air oxidation processes of the synthetic organic chemicals manufacturing industry (SOCMI). Background data and detailed information which support the emission levels achievable are included.

Section C.1 of this appendix presents the VOC emissions test data including individual test descriptions. Section C.2 provides a summary of NO_x emissions from some of the tests. Section C.3 consists of comparisons of various test results and a discussion exploring and evaluating the similarities and differences of these results.

C.1 VOC EMISSIONS TEST DATA

The tests were aimed at evaluating the performance of thermal incinerators when used under varied conditions on the air oxidation process waste streams. The results of this study indicate that 98 weight percent VOC reduction or 20 ppmv by compound exit concentration, whichever is less stringent, is the highest control level currently achievable by all new incinerators, considering available technology, cost, and energy use.[1] This level is expressed in both percent reduction and ppmv to account for the leveling off of exit concentrations as inlet concentrations drop. This level can be achieved by incinerator operation at conditions which include a maximum of 1600°F and 0.75 second residence time. The 98 percent level can frequently be achieved at lower combustion temperatures.

Three sets of test data are available. These sets consist of field unit data from tests conducted by EPA and by chemical companies and of lab-scale incinerator data from tests by Union Carbide.

C.1.1 Chemical Company Test Data

These data are from tests performed by chemical companies on incinerators at three air oxidation units: the Petro-tex oxidative butadiene unit at Houston, Texas, the Koppers maleic anhydride unit at Bridgeville, Pennsylvania, and the Monsanto acrylonitrile unit at Alvin, Texas.

Stack Gas

The stack gas samples are collected via a tee on a long stainless steel probe which can be inserted into the stack at nine different locations. These gas samples are collected in 30-50 cc syringes.

The gas samples are then transferred to a smaller 1 cc syringe via a small glass coupling device sealed at both ends with a rubber grommet. The 1-cc samples can then be injected into a chromatograph for hydrocarbon analysis. A Varian 1700 chromatograph is used, having a 1/8-in. x 6-ft column packed with 5A molecular sieves and a 1/4-in. x 4-ft column packed with glass beads connected in series with a bypass before and after the molecular sieve column, controlled by a needle valve to split the sample. The data are reported as ppm total HC, ppm methane, and ppm non-methane hydrocarbons (NMHC). The CO content in the stack is determined by using a Kitagawa sampling probe. The O_2 content in the stack is determined via a Teledyne O_2/combustible analyzer.

3. Test Results - Petro-tex has been involved in a modification plan for its 'Oxo' incinerator unit after startup. The facility was tested by the company after each major modification was made to determine the impact of these changes on the VOC destruction efficiency. The incinerator showed improved performance after each modification and the destruction efficiency increased from 70 percent to well above 98 percent. Table C-1 provides a summary of these test results. The type of modifications made in the incinerator were as follows:

November 1977

Test data prior to these changes showed the incinerator was not destroying hydrocarbons as well as it should (VOC destruction efficiency as low as 70 percent), so the following changes were made:

1. Moved the duct burner baffles from back of the burner to the front.
2. Installed spacers to create a continuous slot for supplemental air to reduce the air flow through the burner pods.
3. Installed plates upstream of the burners so that ductwork matches burner dimensions.
4. Cut slots in recycle duct to reduce exit velocities and improve mixing with Oxo waste gas.

TABLE C-1. THERMAL INCINERATOR FIELD TEST DATA

Company & Location	Type of Process	Production Rate During Test Waste Gas Flow (Inlet) scfm	Number of Tests or Sets	Test Date	Supplemental Fuel & Amount Used (scfm)	Residence Time (Seconds)	Incineration Temperature (°F)	Inlet VOC (ppmv)	Outlet VOC (ppmv)	VOC Destruction Efficiency by Weight
Petro-tex Chemical Corp., Houston, TX	Butadiene	7,250	Set 1	5/25/77	Natural Gas 1400	0.6	1400	10,300	1000	70.3
		15,617	Set 2	9/09/77	1467	0.6	1400	10,650	215	94.1
		20,750	Set 3	12/01/77	900	0.6	1400	10,650	215	94.1
		15,867	Set 4	4/19/78	1175	0.6	1400	10,300	10	99.6
		12,500	Set 5	9/27/78	1176	0.6	1400	10,300	10	99.6
		Avg. Combustion Air: 49,333								
Koppers Co., Inc. Bridgeville, PA	Maleic Anhydride	33,200 Air: 8000	Set 1	11/02/77	Natural Gas	0.6	"Below 2000"	834	7	98.96
		24,200 Air: 2000	Set 2	11/16/77		0.6		834	8	98.96
Monsanto Chemical Intermediates Co., Alvin, TX	Acrylonitrile	75,000 (Avg.)	Unit 1	12/16/77	Natural Gas	N/A	Confidential	Confidential	25	>99
			Unit 2	12/16/77		N/A			47	>99
Denka, Houston, TX	Maleic Anhydride	33,000 (70% of total capacity)	3	3/21/78	1060 (gas)	0.6	1400	950	13	98.5
				3/22/78	1060	0.6	1400	950	13	98.5
				3/23/78	1060	0.6	1400	950	13	98.5
Rohm & Haas, Deer Park, TX	Acrylic Acid & Esters	Each 52,500 (12,500 tank farm vent (TVF))	Set 1 3	3/78	900 (gas)	1.0	1425	TVF 2,580 OXV 11,600	1330	82.6
			Set 2 4	3/78	900	1.0	1510	TVF 2,600 OXV 12,800	150	98.3
		(40,000 oxidizer vent (OXV))	Set 3 1	3/78	900	1.0	1545	TVF 2,410 OXV 12,200	25	99.7
Union Carbide Corp., Taft, LA	Acrylic Acid & Acrylate Esters	20,600	Set 1 6	12/78	Natural Gas	2-3	1160	11,900	243	96.1
			Set 2 3	12/78		2-3	1475	11,900	10	99.9

C.1.1.1 Petro-Tex Test Data[2]

1. Facility and Control Device - The Petro-tex incinerator for the 'Oxo' butadiene process is designed to treat 48,000 scfm waste gas containing about 4000 ppm hydrocarbon and 7000 ppm carbon dioxide. The use of the term hydrocarbon in this discussion indicates that besides VOC, it may include non-VOC such as methane. The waste gas treated in this system results from air used to oxidize butene to butadiene. The waste gas, after butadiene has been recovered in an oil absorption system, is combined with other process waste gas and fed to the incinerator. The waste gas enters the incinerator between seven vertical Coen duct burner assemblies. The incinerator design incorporates flue gas recirculation and a waste heat boiler. The benefit achieved by recirculating flue gas is to incorporate the ability to generate a constant 100,000 lbs/hr of 750 psi steam with variable waste gas flow.[3] The waste gas flow can range from 10 percent to 100 percent of design production rate.

The incinerator measures 72 feet by 20 feet by 8 feet, with an average firebox cross-sectional area of 111 square feet. The installed capital cost was $2.5 million.

The waste gas stream contains essentially no oxygen; therefore, significant combustion air must be supplied. This incinerator is fired with natural gas which supplies 84 percent of the firing energy. The additional required energy is supplied by the hydrocarbon contamination of the waste gas stream. Figure C-1 gives a rough sketch of this unit.

2. Sampling and Analytical Techniques

Waste Gas

The waste gas sampling was performed with integrated bags. The analysis was done on a Carle analytical gas chromatograph having the following columns:

1. 6-ft OPN/PORASIL[R] (80/100).
2. 40-ft 20 percent SEBACONITRILE[R] on gas chrom. RA 42/60.
3. 4-ft PORAPAK[R] N 80/100.
4. 6-ft molecular sieve bx 80/100.

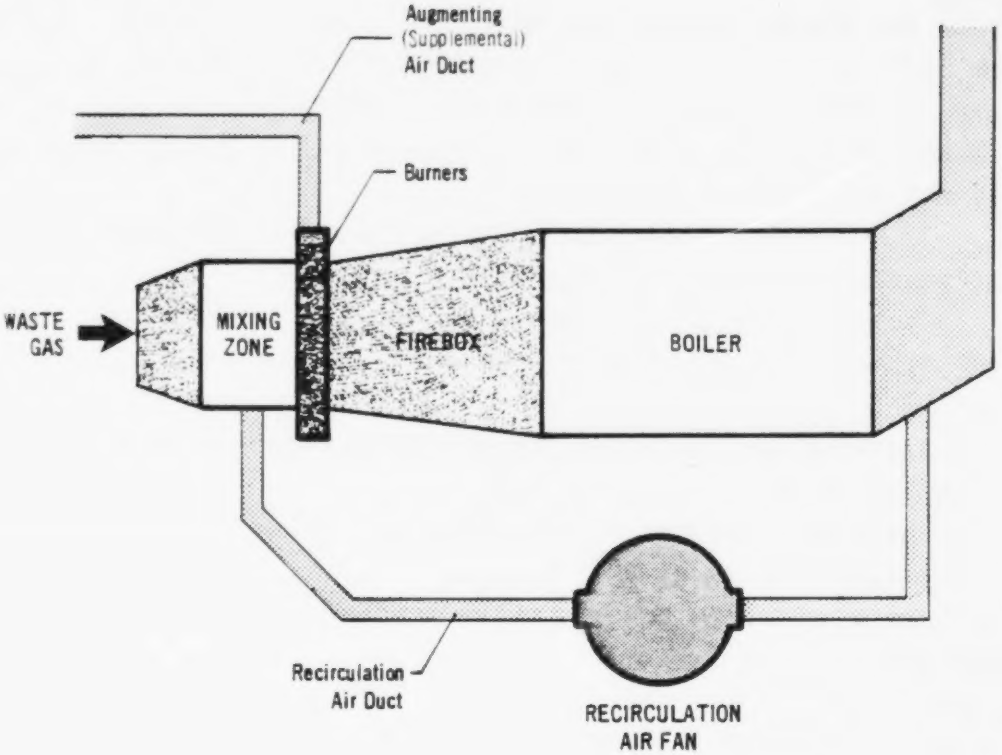

Augmenting
(Supplemental)
Air Duct
Burners
WASTE GAS
MIXING ZONE
FIREBOX
BOILER
Recirculation Air Duct
RECIRCULATION AIR FAN

Figure C-1. Petro-Tex oxo unit incinerator.

5. Installed balancing dampers in augmenting (supplemental) air plenums, top and bottom.

6. Installed balancing dampers in three of the five sections of the recycle duct transition.

7. Cut opening in the recirculation duct to reduce the outlet velocities.

March 1978

After the November changes were made, a field test was made in December 1977, which revealed that the incinerator VOC destruction efficiency increased from 70.3 percent to 94.1 percent. However, it still needed improvement. After much discussion and study the following changes were made in March 1978:

1. Took the recirculation fan out of service and diverted the excess forced draft air into the recirculation duct.

2. Sealed off the 5-1/2-in. wide slots adjacent to the burner pods and removed the 1/2-in. spacers which were installed in November 1977.

3. Installed vertical baffles between the bottom row of burner pads to improve mixing.

4. Installed perforated plates between the five recirculation ducts for better Oxo waste gas distribution.

5. Cut seven 3-in. wide slots in the recycle duct for better secondary air distribution.

July 1978

After the March 1978 changes, a survey in April 1978, showed the Oxo incinerator to be performing very well (VOC destruction efficiency of 99.6 percent) but with a high superheat temperature of ~850°F. So, in July 1978, some stainless steel shields were installed over the superheater elements to help lower the superheat temperature. A subsequent survey in September 1978, showed the incinerator to still be destructing 99.6 percent VOC and with a lower superheat temperature (~750°F).

This study pointed out that mixing is a critical factor in efficiency and that incinerator adjustment after startup is the most feasible and efficient means of improving mixing and thus, the destruction efficiency.

C.1.1.2 Koppers Test Data[4]

1. Facility and Control Device - The Koppers incinerator is actually a boiler adapted to burn gaseous wastes from maleic anhydride unit. The boiler is designed to operate at a temperature of 2000°F and a residence time of 0.6 second. Current operating parameters have not been measured, but it is the company's judgement that the boiler now operates somewhat below 2000°F. The flowrate of waste gas to the boiler is usually 32,000 scfm and contains 350 lbs/hr benzene, 2850 lbs/hr carbon monoxide, 22,100 lbs/hr oxygen, 6434 lbs/hr water, and 105,104 lbs/hr nitrogen. While these values are typical for the system, they vary throughout the production cycle. The boiler is fired with natural gas.

2. Sampling and Analytical Techniques - Different methods were used for inlet and outlet sampling. Although integrated samples were used for the outlet, gas bottle samples were used for the inlet. Such a sampling technique would likely give a low bias to the measured inlet VOC concentration.

The inlet concentration was taken to be the average of all maleic reactor offgas measurements made. There were four samples taken, and the results were 600 ppmv, 1172 ppmv, 600 ppmv, and 964 ppmv for an average of 834 ppmv benzene. (These values are not boiler inlet values since they were collected prior to the introduction of the additional combustion air.) This wide range of benzene values indicates the great deal of variability inherent in efficiency calculations employing such a sampling technique.

For the June 1978 tests, samples of stack gas were taken in glass bottles by plant chemists and analyzed at Koppers' Monroeville Research Center by direct injection to a gas chromatograph with flame ionization detector. The November 1977, method used specially-designed charcoal adsorption tubes, instead of impingers, in a United States Environmental Protection Agency-type sampling train. The charcoal was eluted with CS_2 and the eluent analyzed by gas chromatography.

3. Test Results - One test run of the Koppers data indicates 97.2 percent efficiency at 1800°F. However, the entire Koppers test is disregarded as not demonstrably accurate because of the poor sampling

technique. Grab samples employed in obtaining inlet gas could give a low bias to the measured inlet VOC concentration. Therefore, the calculated VOC destruction efficiency would be artificially low. Table C-1 provides a summary of these test results.

C.1.1.3 Monsanto Test Data[5]

1. Facility and Control Device - The Monsanto incinerator burns both liquid and gaseous wastes from the acrylonitrile unit and is termed an absorber vent thermal oxidizer. Two identical oxidizers are employed. The primary purpose of the absorber vent thermal oxidizers is hydrocarbon emission abatement.

Acrylonitrile is produced by feeding propylene, ammonia, and excess air through a fluidized, catalytic bed reactor. In the process, acrylonitrile, acetonitrile, hydrogen cyanide, carbon dioxide, carbon monoxide, water, and other miscellaneous organic compounds are produced in the reactor. The columns in the recovery section separate water and crude acetonitrile as liquids. Propane, unreacted propylene, unreacted air components, some unabsorbed organic products, and water are emitted as a vapor from the absorber column overhead. The crude acrylonitrile product is further refined in the purification section to remove hydrogen cyanide and the remaining hydrocarbon impurities.

The organic waste streams from this process are incinerated in the absorber vent thermal oxidizer at a temperature and residence time sufficient to reduce stack emissions below the required levels. The incinerated streams include (1) the absorber vent vapor (propane, propylene, CO, unreacted air components, unabsorbed hydrocarbons), (2) liquid waste acetonitrile (acetonitrile, hydrogen cyanide, acrylonitrile), (3) liquid waste hydrogen cyanide, and (4) product column bottoms purge (acrylonitrile, some organic heavies). The two separate acrylonitrile plants at Chocolate Bayou, employ identical thermal oxidizers.

Each thermal oxidizer is a horizontal, cylindrical, saddle-supported, end-fired unit consisting of a primary burner vestibule attached to the main incinerator shell. Each oxidizer measures 18 feet in diameter by 36 feet in length.

The thermal oxidizer is provided with special burners and burner guns. Each burner is a combination fuel-waste liquid unit. The absorber vent stream is introduced separately into the top of the burner vestibule. The flows of all waste streams are metered and sufficient air is added for complete combustion. Supplemental natural gas is used to maintain the operating temperature required to combust the organics and to maintain a stable flame on the burners during minimum gas usage. Figure C-2 gives a plan view of the incinerator.

2. Sampling and Analytical Techniques

Feed Stream and Effluent

The vapor feed streams (absorber vent) to the thermal oxidizer and the effluent gas stream are sampled and analyzed using a modified analytical reactor recovery run method. The primary recovery run methods are Sohio Analytical Laboratory Procedures.

The modified method involves passing a measured amount of sample gas through three scrubber flasks containing water and catching the scrubbed gas in a gas sampling bomb. The samples are then analyzed with a gas chromatograph and the weight percent of the components is determined.

Stack Gas

Figure C-3 shows the apparatus and configuration used to sample the stack gas. It consists of a line of the sample valve to the small water-cooled heat exchanger. The exchanger is then connected to a 250 ml sample bomb used to collect the unscrubbed sample. The bomb is then connected to a pair of 250 ml bubblers, each with 165 ml of water in it. The scrubbers, in turn, are connected to another 250 ml sample bomb used to collect the scrubbed gas sample which is connected to a portable compressor. The compressor discharge then is connected to a wet test meter that vents to the atmosphere.

After assembling the apparatus, the compressor is turned on and it draws gas from the stack and through the system at a rate of ~0.2 ft^3/min. Sample is drawn until at least 10 ft^3 have passed through the scrubbers. After 10 ft^3 has been scrubbed, the compressor is shutdown and the unscrubbed bomb is analyzed for CH_4, C_2's, C_3H_6, and C_3H_8, the scrubbed bomb is analyzed for N_2, air, O_2, CO_2, and CO, and the bubbler liquid is analyzed for acrylonitrile, acetonitrile, hydrogen cyanide, and total organic carbon. The gas samples are analyzed by gas chromatography.

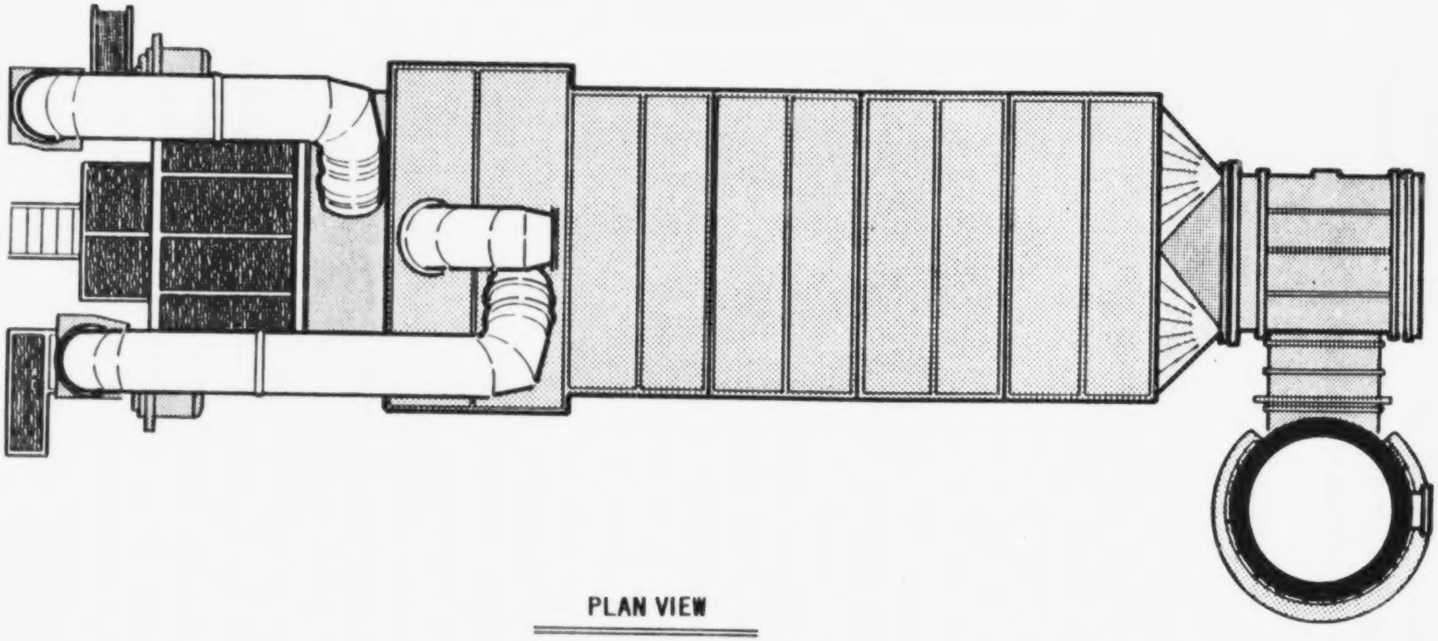
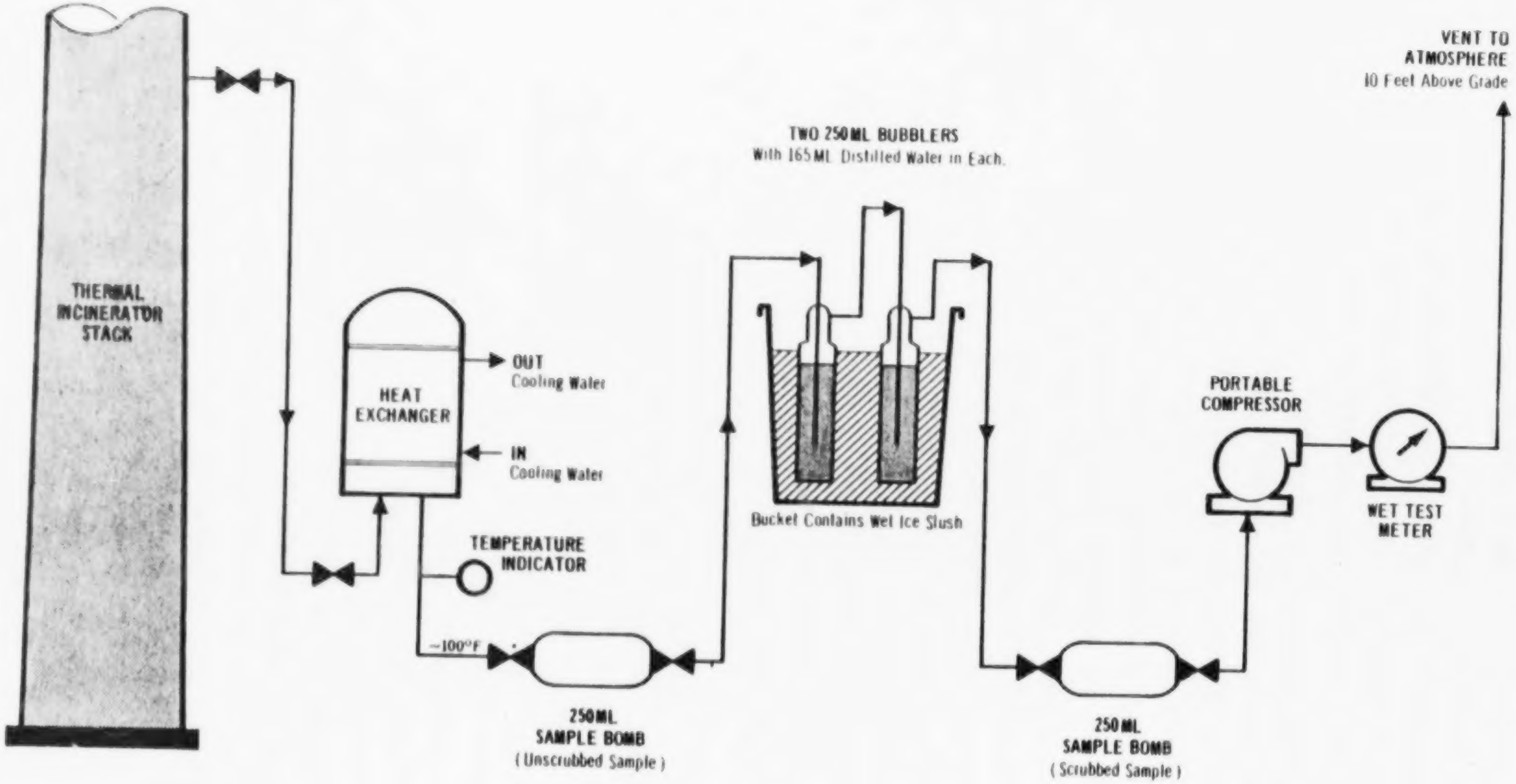


Figure C-2. Off-gas incinerator, Monsanto Co., Chocolate Bayou Plant.


THERMAL INCINERATOR STACK
HEAT EXCHANGER
OUT Cooling Water
IN Cooling Water
TEMPERATURE INDICATOR
~100°F
250ML SAMPLE BOMB (Unscrubbed Sample)
TWO 250ML BUBBLERS With 165ML Distilled Water in Each.
Bucket Contains Wet Ice Slush
250ML SAMPLE BOMB (Scrubbed Sample)
PORTABLE COMPRESSOR
WET TEST METER
VENT TO ATMOSPHERE 10 Feet Above Grade

NOTE: From Exchanger Process Outlet, All Lines are Vacuum Tubing.

Figure C-3. Thermal incinerator stack sampling system.

For the liquid samples, acrylonitrile and acetonitrile are analyzed by gas chromatography; hydrogen cyanide (HCN) is by titration; and total organic carbon (TOC) is by a carbon analysis instrument.

3. Test Results - Monsanto's test results show efficiencies well above 98 percent, however, the parameters at which it is achieved are confidential. All other known conditions are presented in Table C-1.

C.1.2 Environmental Protection Agency (EPA) Test Data

The EPA test study represents the most in-depth work available. These data show the combustion efficiencies for full-scale incinerators on air oxidation vents at three chemical plants. Data includes inlet/outlet tests on large incinerators, two at acrylic acid plants, and one at a maleic anhydride plant. The tests measured inlet and outlet VOC by compound at different temperatures, and the reports include complete test results, process rates, and test method descriptions. The three plants tested are the Denka, Houston, Texas, maleic anhydride unit and the Rohm and Haas, Deer Park, Texas, and Union Carbide, Taft, Louisiana, acrylic acid units. The data from Union Carbide include test results based on two different incinerator temperatures. The data from Rohm and Haas include results for three temperatures. In all tests, bags were used for collecting integrated samples and a GC/FID was used for organic analysis.

C.1.2.1 Denka Test Data[6]

1. Facility and Control Device - The Denka maleic anhydride facility has a nameplate capacity of 23,000 Mg/yr (50 million lbs/yr). The plant was operating at about 70 percent of capacity when the sampling was conducted. The plant personnel did not think that the lower production rate would seriously affect the validity of the results.

Maleic anhydride is produced by vapor-phase catalytic oxidation of benzene. The liquid effluent from the absorber, after undergoing recovery operations, is about 40 weight percent aqueous solution of maleic acid. The absorber vent is directed to the incinerator. The thermal incinerator uses a heat recovery system to generate process steam and uses natural gas as supplemental fuel. The size of the combustion chamber is 2195 ft^2. There are three thermocouples used to sense the flame temperature, and these are averaged to give the temperature recorded in the control room. A rough sketch of the combustion chamber is provided in Figure C-4.

2. Sampling and Analytical Techniques

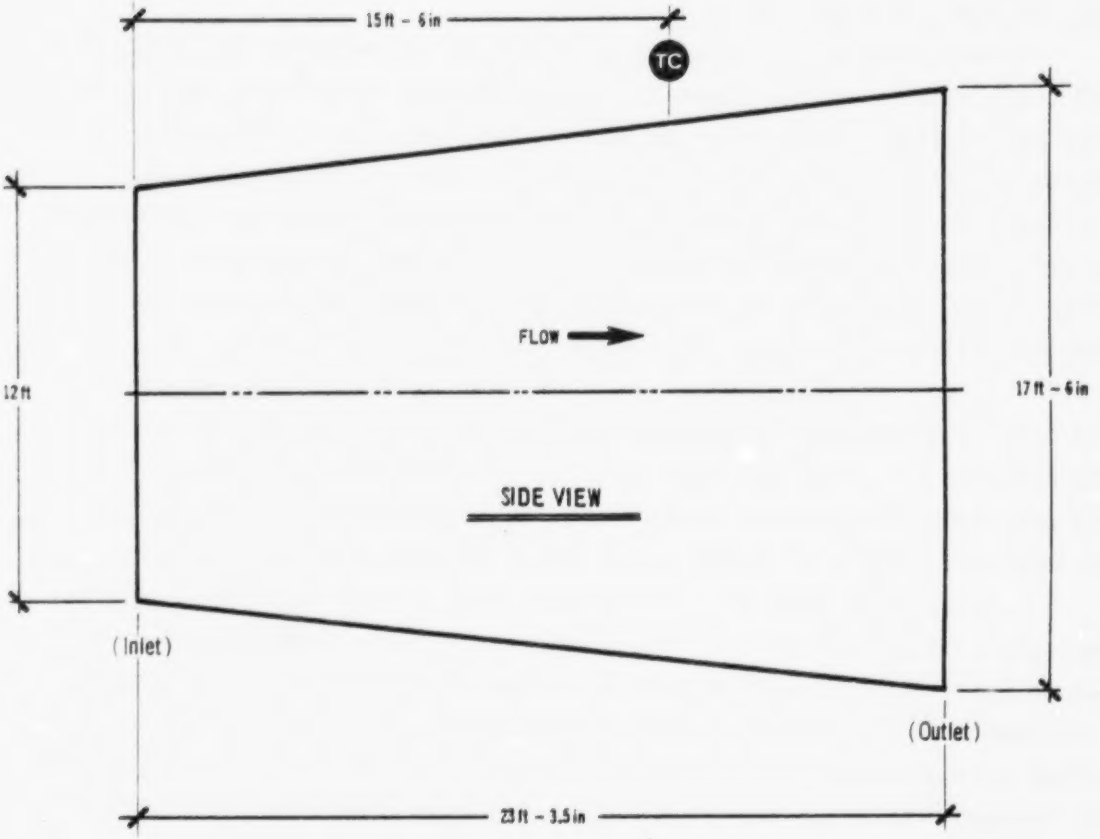
THC, Benzene, Methane, and Ethane

The gas samples were obtained according to the September 27, 1977, EPA draft benzene method. Seventy-liter aluminized Mylar^R bags were used with sample times of two to three hours. The sample box and bag were heated to approximately 66^{o}C (150^{o}F) using an electric drum heater and insulation. During Run 1-Inlet, the variac used to control the temperature malfunctioned so the box was not heated for this run. A stainless steel probe was inserted into the single port at the inlet and connected to the gas bag through a "tee". The other leg of the "tee" went to the total organic acid (TOA) train. A Teflon^R line connected the bag and the "tee". A stainless steel probe was connected directly to the bag at the outlet. The lines were kept as short as possible and not heated. The boxes were transported to the field lab immediately upon completion of sampling. They were heated until the GC analyses were completed.

A Varian model 2440 gas chromatograph with a Carle gas sampling valve, equipped with two cm^3 matched loops, was used for the integrated bag analysis. The SP-1200/Bentone 34 column was operated at 80^{o}C. The instrument has a switching circuit which allows a bypass around the column through a capillary tube for THC response. The response curve was measured daily for benzene (5, 10, and 50 ppm standards) with the column and in the bypass (THC) mode. The THC mode was also calibrated daily with propane (20, 100, and 2000 ppm standards). The calibration plots showed moderate nonlinearity. For sample readings which fell within the range of the calibration standards, an interpolated response factor was used from a smooth curve drawn through the calibration points. For samples above or below the standards, the response factor of the nearest standard was assumed. THC readings used peak height and column readings used area integration measured with an electronic "disc" integrator.

CO

Analysis for these constituents was done on samples drawn from the integrated gas bag used in THC, benzene, methane, and ethane. Carbon


15 ft - 6 in
TC
FLOW
12 ft
17 ft - 6 in
SIDE VIEW
(Inlet)
(Outlet)
23 ft - 3.5 in

There are Three Thermocouples Spaced Evenly Across the Top of the Firebox.

The Width of the Firebox is 6 ft – 6 in.

Figure C-4. Incinerator combustion chamber.

monoxide analysis was done following the GC analyses using EPA Reference Method 10 (Federal Register, Vol. 39, No. 47, March 8, 1974). A Beckman Model 215 NDIR analyzer was used to analyze both the inlet and outlet samples.

Duct Temperature, Pressure, and Velocity

Duct temperature and pressure values were obtained from the existing inlet port. A thermocouple was inserted into the gas sample probe for the temperature while a water manometer was used for the pressure readings. These values were obtained at the conclusion of the sampling period.

Temperature, pressure, and velocity values were obtained for the outlet stack. Temperature values were obtained by thermocouple during the gas sampling. Pressure and velocity measurements were taken according to EPA Reference Method 2 (Federal Register, Vol. 42, No. 160, August 18, 1977). These values also were obtained at the conclusion of the sampling period.

2. Test Results - The Denka incinerator achieves greater than 98 percent reduction at 1400°F and 0.6 second residence time. These results suggest that the recommended 98 percent control level is achievable by properly maintained and operated new incinerators, for which the operating conditions are less stringent than 1600°F and 0.75 second. Table C-1 provides a summary of these test results.

C.1.2.2 Rohm and Haas Test Data[7]

1. Facility and Control Device - The Rohm and Haas plant in Deer Park, Texas, produces acrylic acid and ester. The capacity of this facility has been listed at 400 million lbs/yr of acrylic monomers. Acrylic esters are produced using propylene, air, and alcohols, with acrylic acid produced as an intermediate. Acrylic acid is produced directly from propylene by a vapor-phase catalytic air oxidation process. The reaction product is purified in subsequent refining operations. Excess alcohol is recovered and heavy end by-products are incinerated. This waste incinerator is designed to burn offgas from the two absorbers. In addition, all process vents (from extractors, vent condensers, and tanks) which might be a potential source of gaseous emissions are collected in a suction vent system and normally sent to the incinerator. An

organic liquid stream generated in the process is also burned, thereby providing part of the fuel requirement. The remainder is provided by natural gas. Combustion air is added in an amount to produce six percent oxygen in the effluent. Waste gases are flared during maintenance shutdowns and severe process upsets. The incinerator unit was tested because it operates at relatively shorter residence times (0.75-1.0 seconds) and higher combustion temperatures (1200°-1560°F) than most existing incinerators.

The total installed capital cost of the incinerator was $4.7 million. The estimated operating cost due to supplemental natural gas use is $0.9 million per year.

2. Sampling and Analytical Techniques - Samples were taken simultaneously at a time when propylene oxidations, separations, and esterifications were operating smoothly and the combustion temperature was at a steady state. Adequate time was allowed between the tests conducted at different temperatures for the incinerator to achieve steady state. Bags were used to collect integrated samples and a GC/FID was used for organic analysis.

3. Test Results - VOC destruction efficiency was determined at three different temperatures: 1425°F, 1510°F, and 1545°F. Efficiency is found to increase with temperature and, except for 1425°F, it is above 98 percent. Test results are summarized in Table C-1. These tests were for residence times greater than 0.75 second. However, theoretical calculations show that greater efficiency would be achieved at 1600°F and 0.75 second than at the longer residence times, but lower temperatures represented in these tests.

C.1.2.3 Union Carbide (UCC) Test Data[8]

1. Facility and Control Device - The capacities for the UCC acrylates facilities are about 200 million lbs/yr of acrolein, acrylic acid, and esters. Acrylic acid comprises 130 million lbs/yr of this total. Ethyl acrylate capacity is 90 million lbs/yr. Total heavy ester capacities (such as 2-ethyl-hexyl acrylate) are 110 million lbs/yr. UCC considers butyl acrylate a heavy ester.

The facility was originally built in 1969 and utilized British Petroleum technology for acrylic acid production. In 1976 the plant was converted to a technology obtained under license from Sohio.

The thermal incinerator is one of the two major control devices used in acrylic acid and acrylate ester manufacture. The UCC incinerator was installed in 1975 to destroy acrylic acid and acrolein vapors. This unit was constructed by John Zink Company for an installed cost of $3 million and incorporates a heat recovery unit to produce process steam at 600 psig. The unit operates at a relatively constant feed input and supplements the varying flow and fuel value of the streams fed to it with inversely varying amounts of fuel gas. Energy consumption averages 52.8 million Btu/hr instead of the designed level of 36-51 million Btu/hr. The operating cost in 1976, excluding capital depreciation, was $287,000. The unit is run with nine percent excess oxygen instead of the designed three to five percent excess oxygen. The combustor is designed to handle a maximum of four percent propane in the oxidation feed.

Materials of construction of a non-return block valve in the 600 psig steam line from the boiler section requires that the incinerator be operated at 1200°F instead of the designed 1800°F. The residence time is three to four seconds.

2. Sampling and Analytical Procedures - The integrated gas samples were obtained according to the September 27, 1977, EPA draft benzene method.

Each integrated gas sample was analyzed on a Varian Model 2400 gas chromatograph with FID, and a heated Carle gas sampling valve with matched 2 cm^3 sample loops. A valved capillary bypass is used for total hydrocarbon (THC) analyses and a 2 m, 1/8-in., OD nickel column with PORAPAK^R P-S, 80-100 mesh packing is used for component analyses.

Peak area measurements were used for the individual component analyses. A Tandy TRS-80, 48K floppy disc computer interfaced via the integrator pulse output of a Linear Instruments Model 252A recorder acquired, stored, and analyzed the chromatograms.

The integrated gas samples were analyzed for oxygen and carbon dioxide by duplicate Fyrite readings. Carbon monoxide concentrations were obtained using a Beckman Model 215A nondispersive infrared (IR) analyzer using the integrated samples. A three-point calibration (1000, 3000, and 10,000 ppm CO standards) was used with a linear-log curve fit.

Stack traverses for outlet flowrate were made using EPA Methods 1 through 4 (midget impingers) and NO_x was sampled at the outlet using EPA Method 7.

3. Test Results - VOC destruction efficiency was determined at two different temperatures. Table C-1 provides a summary of these test results. Efficiency was found to increase with temperature. At 1475°F, the efficiency was well above 99 percent. These tests were, again, for residence times greater than 0.75 second. However, theoretical calculations show that greater efficiency would be achieved at 1600°F and 0.75 second than at the longer residence times but lower temperatures represented in these tests.

All actual measurements were made as parts per million (ppm) of propane with the other units reported derived from the equivalent values. The values were measured by digital integration.

The incinerator combustion temperature for the first six runs was about 1160°F. Runs 7 through 9 were made at an incinerator temperature of about 1475°F. Only during Run 3 was the acrolein process operating. The higher temperature caused most of the compounds heavier than propane to drop below the detection limit due to the wide range of attenuations used, nearby obscuring peaks, and baseline noise variations. The detection limit ranges from about 10 ppb to 10 ppm, generally increasing during the chromatogram, and especially near large peaks. Several of the minor peaks were difficult to measure. However, the compounds of interest, methane, ethane, ethylene, propane, propylene, acetaldehyde, acetone, acrolein, and acrylic acid, dominate the chromatograms. Only acetic acid was never detected in any sample.

The probable reason for negative destruction efficiencies for several light components is generation by pyrolysis from other components. For instance, the primary pyrolysis products of acrolein are carbon monoxide and ethylene. Except for methane and, to a much lesser extent, ethane and propane, the fuel gas cannot contribute hydrocarbons to the outlet samples.

A sample taken from the inlet line knockout trap showed 6 μg/g of acetaldehyde, 25 μg/g of butenes, and 100 μg/g of acetone when analyzed by gas chromatography/flame ionization detection (GC/FID).

C.1.3 Union Carbide Lab-Scale Test Data[9]

Union Carbide test data show the combustion efficiencies achieved on 15 organic compounds in a lab-scale incinerator operating between 800° and 1500°F and .1 to 2 seconds residence time. The incinerator consisted of a 130 cm, thin bore tube, in a bench-size tube furnace. Outlet analyzers were done by direct routing of the incinerator outlet to a FID and GC. All inlet gases were set at 1000 ppmv.

In order to study the impact of incinerator variables on efficiency, mixing must first be separated from the other parameters. Mixing cannot be measured and thus, its impact on efficiency cannot be readily separated when studying the impact of other variables. The Union Carbide lab work was chosen since its small size and careful design best assured consistent and proper mixing.

The results of this study are shown in Table C-2. These results show moderate increases in efficiency with temperature, residence time, and type of compound. The results also show the impact of flow regime on efficiency.

Flow regime is important in interpreting the Union Carbide lab unit results. These results are significant since the lab unit was designed for optimum mixing and thus, the results represent the upper limit of incinerator efficiency. As seen in Table C-2, the Union Carbide results vary by flow regime. Though some large-scale incinerators may achieve good mixing and plug flow, the worst cases will likely require flow patterns similar to complete backmixing. Thus, the results of complete backmixing would be, relatively, more comparable to those obtained from large-scale units.

C.2 NITROGEN OXIDES (NO_x) EMISSIONS

Nitrogen oxides are derived mainly from two sources: (1) from nitrogen contained in the combustion air called thermal NO_x, and (2) from nitrogen chemically combined in the fuel, called fuel NO_x. In addition, combustion of waste gas containing high levels of nitrogen-containing compounds also may cause increases in NO_x emissions. For fuels containing low amounts of nitrogen, such as natural gas and light distillate oils, thermal NO_x is by far the larger component of total NO_x

TABLE C-2. RESULTS OF DESTRUCTION EFFICIENCY UNDER STATED CONDITIONS (UNION CARBIDE TESTS[a])

		Residence Time/Compound				
			0.75 second			.5 & 1.5 sec
Flow Regime[b]	Temperature (°F)	Ethyl Acrylate	Ethanol	Ethylene	Vinyl Chloride	Ethylene
Two-stage Backmixing	1300	99.9	94.6	92.6	78.6	87.2/27.6
	1400	99.9	99.6	99.3	99.0	98.6/99.8
	1500	99.9	99.9	99.9	99.9	99.9/99.9
	1600	99.9	99.9	99.9	99.9	99.9/99.9
Complete Backmixing	1300	98.9	86.8	84.4	69.9	78.2/91.5
	1400	99.7	96.8	95.6	93.1	93.7/97.8
	1500	99.9	99.0	98.7	98.4	98.0/99.0
	1600	99.9	99.7	99.6	99.6	99.4/99.8
Plug Flow	1300	99.9	99.9	99.5	90.2	97.3/99.9
	1400	99.9	99.9	99.9	99.9	99.9/99.9
	1500	99.9	99.9	99.9	99.9	99.9/99.9
	1600	99.9	99.9	99.9	99.9	99.9/99.9

[a] The results of the Union Carbide work are presented as a series of equations. These equations relate destruction efficiency to temperature, residence time, and flow regime for each of 15 compounds. The efficiencies in this table were calculated from these equations.

[b] Three flow regimes are presented: two-stage backmixing, complete backmixing, and plug flow. Two-stage backmixing is considered a reasonable approximation of actual field units, with complete backmixing and plug flow representing the extremes.

emissions. By contrast, fuel NO_x predominates for heavy oils, coal, and other high-nitrogen fuels such as coal-derived fuels and shale oils.

Thermal oxidizer outlet concentrations of NO_x were measured in seven sets of thermal oxidizer tests conducted at three air oxidation plants. Table C-3 provides a summary of the test results. The test results indicate that NO_x outlet concentrations range from 8 to 200 ppmv (0.015 to 0.37 g/m^3). These values could increase by several orders of magnitude in a poorly designed or operated unit. NO_x samples were obtained according to EPA Reference Method 7.

The maximum outlet NO_x concentration of 200 ppmv was measured at an acrylonitrile plant. The vent stream of this plant contains nitrogeneous compounds. The NO_x concentrations measured at the other two plants, whose vent streams do not contain nitrogeneous compounds, range from 8 to 30 ppmv (0.015 to 0.056 g/m^3).

C.3 COMPARISON OF TEST RESULTS AND THE TECHNICAL BASIS OF THE SOCMI AIR OXIDATION EMISSIONS LIMIT

This section compares various test results, discusses data and findings on incinerator efficiency, and presents the logic and the technical basis behind the choice of the above control level.

A consideration of VOC combustion kinetics leads to the conclusion that at 1600°F and 0.75 second residence time, mixing is the crucial design parameter. Published literature indicates that any VOC can be oxidized to carbon dioxide and water if held at sufficiently high temperatures in the presence of oxygen for a sufficient time. However, the temperature at which a given level of VOC reduction is achieved is unique for each VOC compound. Kinetic studies indicate that there are two slow or rate-determining steps in the oxidation of a compound. The first is the initial reaction in which the original compound disappears. It has been determined that the initial reaction of methane (CH_4) is slower than that of any other nonhalogenated organic compound. Kinetic calculations show that, at 1600°F, 98 percent of the original methane will react in 0.3 seconds. Therefore, any nonhalogenated VOC will undergo an initial reaction step within this time. After the initial step, extremely rapid free radical reactions occur. Finally, each carbon atom will exist as carbon monoxide (CO) before oxidation is complete. The oxidation of CO is the second slow step. Calculations show that, at 1600°F, 98 percent

TABLE C-3. SUMMARY OF RESULTS: NO_x DATA

Company	Number of Sets and/or Number of Runs	Outlet NO_x in Flue Gas (ppmv)
Union Carbide	Set 1 (6)	27
	Set 2 (3)	30
Denka	Set 1	9.3
	Set 2	10.2
	Set 3	8.0
Monsanto	Unit 1	200
	Unit 2	8

of an original concentration of CO will react in 0.05 second. Therefore, 98 percent of any VOC would be expected to undergo the initial and final slow reaction steps at 1600°F in about 0.35 second. It is very unlikely that the intermediate free radical reactions would take nearly as long as 0.4 seconds to convert 98 percent of the organic molecules to CO. Therefore, from a theoretical viewpoint, any VOC should undergo complete combustion at 1600°F in 0.75 second. The calculations on which this conclusion is based have taken into account the low mole fractions of VOC and oxygen which would be found in the actual system. They have also provided for the great decrease in concentration per unit volume due to the elevated temperature. But the calculations assume perfect mixing of the offgas and combustion air. Mixing is therefore identified from a theoretical viewpoint as the crucial design parameter.

The test results both indicate an achievable control level of 98 percent at or below 1600°F and illustrate the importance of mixing. Union Carbide results on lab-scale incinerators indicated a minimum of 98.6 percent efficiency at 1400°F. Since lab-scale incinerators primarily differ from field units in their excellent mixing, these results verified the theoretical calculations. The tests cited in Table C-1 are documented as being conducted on full-scale incinerators controlling offgas from air oxidation process vents of a variety of types of plants. To focus on mixing, industrial units were selected where all variables except mixing were held constant or accounted for in other ways. It was then assumed any changes in efficiency would be due to changes in mixing.

The case most directly showing the effect of mixing is that of Petro-tex incinerator. The Petro-tex data show the efficiency changes due to modifications on the incinerator at two times after startup. These modifications included (1) repositioning baffles, (2) adjusting duct slots and openings in the mixing zone to improve exit velocity, (3) installing new dampers, baffles and perforated plates, and (4) rerouting inlet combustion air. These modifications increased efficiency from 70 percent to over 99 percent, with no significant change in temperature.

A comparison indirectly showing the effect of mixing is that of the Rohm and Haas test versus the Union Carbide lab test as presented in Table C-4. These data compare the efficiency of the Rohm and Haas (R&H)

TABLE C-4. RESULT COMPARISONS OF LAB INCINERATOR vs. ROHM & HAAS INCINERATOR[a]

Compound	Rohm & Haas Incinerator Inlet (lbs/hr)	Rohm & Haas Incinerator Outlet (lbs/hr)	Union Carbide Lab Incinerator Inlet (lbs/hr)	Union Carbide Lab Incinerator Outlet (lbs/hr)
Propane	900	150	71.4	0.64
Propylene	1800[b]	150[b]	142.9	5.6
Ethane	10	375	0.8	3.9
Ethylene	30	190	2.4	3.4
TOTAL	2740	865	217.5	13.54
% VOC Destruction:	68.4%		93.8%	

[a] Table shows the destruction efficiency of the four listed compounds for the Rohm & Haas (R&H) field and Union Carbide (UC) lab incinerators. The R&H results are measured; the UC results are calculated. Both sets of results are based on 1425°F combustion temperature and one second residence time. In addition, the UC results are based on complete backmixing and a four-step combustion sequence consisting of propane to propylene to ethane to ethylene to CO_2 and H_2O. These last two items are worst case assumptions.

[b] Are not actual values. Actual values are confidential. Calculations with actual values give similar results.

incinerator in combusting four specific compounds with that of the Union Carbide lab unit. The lab unit clearly outperforms the R&H unit. The data from both units are based on the same temperature, residence time, and inlet stream conditions. The more complete mixing of the lab unit is judged the cause of the differing efficiencies. The six tests of in-place incinerators do not, of course, cover every feedstock. However, the theoretical discussion given above indicates that any VOC compound should be sufficiently destroyed at 1600°F. More critical than the type of VOC is the VOC concentration in the offgas. This is true because the kinetics of combustion are not exactly first-order at low VOC concentrations. The Petro-tex results are for a butadiene plant, and butadiene offgas tends to be lean in VOC. Therefore, test results support the validity of the standard for lean streams.

The EPA, Union Carbide, and Rohm and Haas tests were for residence times greater than 0.75 second. However, theoretical calculations show that greater efficiency would be achieved at 1600°F and 0.75 second than at the longer residence times but lower temperatures represented in these two tests. The data on which the standard is based is test data for similar control systems: thermal incineration at various residence times and temperatures. If 98 percent VOC reduction can be achieved at a lower temperature, then according to kinetic theory it can certainly be achieved at 1600°F, other conditions being equal.

A control efficiency of 98 percent VOC reduction, or 20 ppmv by compound, whichever is less stringent, represents the highest acheivable control level for all new incinerators, considering available technology, cost and energy use. This is based on incinerator operation at 1600°F and on adjustment of the incinerator after start-up. The 20 ppmv (by compound) level was chosen after three different incinerator outlet VOC concentrations, 10 ppmv, 20 ppmv, and 30 ppmv, were analyzed. In addition to the incinerator tests cited earlier in this Appendix, data from over 200 tests by Los Angeles County (L.A.) on various waste gas incinerators were considered in choosing the 20 ppmv level. However, the usefulness of the L.A. data was limited by three factors: (1) the incinerators tested are small units designed over a decade ago; (2) the units were designed, primarily, for use on coating operations; and (3) the units were designed to meet a regulation requiring only 90 percent VOC reduction.

The 10 ppmv level was judged to be too stringent. Two of the six non-L.A. tests and 65 percent of the L.A. tests fail this criteria. Consideration was given to the fact that many of the units tested were below $1600^{0}F$ and did not have good mixing. However, due to the large percent that failed, it is judged that even with higher temperatures and moderate adjustment, a large number of units would still not meet the 10 ppmv level.

The 20 ppmv level was judged to be attainable. All of the non-L.A. and the majority of the L.A. units met this criteria. There was concern over the large number of L.A. tests that failed, i.e. 43 percent. However, two factors outweighed this concern.

First, all of the non-L.A. units met the criteria. This is significant since, though the L.A. units represent many tests, they represent the same basic design. They all are small units designed over a decade ago to meet a rule for 90 percent reduction. They are for similar applications for the same geographic region designed in many cases by the same vendor. Thus, though many failed, they likely did so due to common factors and do not represent a wide spread inability to meet 20 ppmv.

Second, the difference between 65 percent failing 10 ppmv and 43 percent failing 20 ppmv is larger than a direct comparison of the percentages would reveal. At 20 ppmv, not only did fewer units fail, but those that did miss the criteria did so by a smaller margin and would require less adjustment. Dropping the criteria from 10 ppmv to 20 ppmv drops the failure rate by 20 percent, but is judged to drop the overall time and cost for adjustment by over 50 percent.

The difference between the two levels is even greater when the adjustment effort for the worst case is considered. The crucial point is how close a 10 ppm level pushes actual field unit efficiencies to those of the lab unit. Lab unit results for complete backmixing indicate that a 10 ppmv level would force field units to almost match lab unit mixing. A less stringent 20 ppmv level increases the margin allowed for nonideal incinerator operation, especially for the worst cases. Given that exponential increase may occur in costs to improve mixing as field units approach lab unit efficiencies, a drop from 10 ppmv to 20 ppmv may decrease costs to improve mixing in the worst case by an order of magnitude.

The 30 ppmv level was judged too lenient. The only data indicating such a low efficiency was from L.A. All other data showed 20 ppmv. The non-L.A. data and lab data meet 20 ppmv and the Petro-tex experience showed that moderate adjustment can increase efficiency. In addition, the L.A. units were judged to have poor mixing. The mixing deficiencies were large enough to mask the effect of increasing temperature. Thus, it is judged that 20 ppmv could be reached with moderate adjustment and that a 30 ppmv level would represent a criteria not based on the best available units, considering cost, energy, and environmental impact.

C.4 REFERENCES FOR APPENDIX C

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APPENDIX D: MONITORING AND PEFORMANCE TEST METHODS

APPENDIX D: MONITORING AND PERFORMANCE TEST METHODS

D.1 INTRODUCTION

The proposed air oxidation New Source Performance Standard (NSPS) divides air oxidation processes into two groups. One group of facilities is required under the proposed standard, to reduce VOC emissions by 98 weight percent or to 20 ppm (volume, by compound), whichever is less stringent. Standard measurement methods should be used to determine the VOC reduction. The second group is not required to reduce VOC emissions under the proposed standard. As discussed in Chapter 8 and Appendix E, the two groups of facilities are distinguished by a cutoff level of total resource-effectiveness (TRE). An index value of TRE can be associated with each air oxidation vent stream for which the offgas characteristics of flowrate, hourly VOC emissions, and net heating value are known. The proposed standard would require that measurements be made to determine whether a source has a TRE index value above or below the cutoff level. In this case, measurements are needed to determine the flowrate, hourly VOC emissions, and net heating value of each air oxidation process vent stream.

The purpose of this appendix is to discuss and present measurement methods acceptable for determination of (1) VOC reduction efficiency, (2) hourly VOC emissions, and (3) stream net heating value.

D.2 VOC REDUCTION EFFICIENCY MEASUREMENT

Numerous methods exist for the measurement of organic emissions. Among these methods are gas chromatograph (GC), direct flame ionization detection (FID), and EPA Reference Method 25 (EPA 25) -- Determination of Total Gaseous Non-Methane Organic Emissions as Carbon. Each method has advantages and disadvantages. Of the three procedures, GC has the distinct advantage of identifying and quantifying the individual compounds are that GC systems are expensive and determination of the column required and analysis of samples can be time consuming.

The FID technique is the simplest procedure. However, the FID responds differently to various organic compounds and can yield highly biased results depending upon the compounds involved. Another disadvantage of the FID is that a separate methane measurement is required to determine non-methane organics. The direct FID procedure does not identify or quantify individual compounds.

Method 25 sampling and analysis provides a single non-methane organic measurement on a carbon basis; this is convenient for establishing control device efficiencies on a consistent basis. However, EPA 25 does not provide any qualitative or quantitative information on individual compounds present.

D.2.1 Emission Measurement Tests

Emission tests[1,2] using these three methods were conducted for the Office of Air Quality Planning and Standards (OAQPS) at two air oxidation facilities (acrylic acid production). In addition, a laboratory study[3] was conducted by Midwest Research Institute (MRI) under EPA contract to investigate the applicability of Method 25 to measurement of emissions from air oxidation processes.

Table D-1 summarizes the data obtained at the two field tests. For each test method, the calculated (average) control device efficiencies are presented; the average inlet and outlet concentrations (ppm volume as carbon) are also presented. Note that the control device efficiencies are calculated from mass emission rates (not presented in Table D-1) since the addition of significant amounts of combustion air at these sources effectively reduces the outlet concentrations. The inlet and outlet concentrations are presented in Table D-1 only to provide the reader with an idea of the concentration levels involved.

In Table D-1, four basic data sets are provided - data for two incincerator operating conditions at each of two different facilities. In general, the calculated efficiencies for the different test methods are very similar and are in the 94-99 percent range. However, this range is significant when dealing with a standard of 98 percent control efficiency. One notable deviation from this general conclusion is Plant A, Condition 1, where the FID yielded a calculated efficiency of 93 percent; this was significantly higher than either the GC or EPA 25 which yielded efficiencies of 71 and 77 percent, respectively. The higher calculated efficiency for the FID was a result of lower outlet emission rates measured by the FID. EPA 25 usually gave the lowest calculated efficiencies, followed by the GC, and then the FID procedures. Although Method 25

Table D-1
Emission Measurement Test Results

METHOD		TOTAL ORGANIC Average concentration (ppm C_1) inlet	TOTAL ORGANIC Average concentration (ppm C_1) outlet	TOTAL ORGANIC Control efficiency (percent)[a]	NON-METHANE ORGANIC Average concentration (ppm C_1) inlet	NON-METHANE ORGANIC Average concentration (ppm C_1) outlet	NON-METHANE ORGANIC Control efficiency (percent)[a]
Plant A							
Condition 1:	GC/FID[b]				28330	5413	71.2
	FID[c,d]	29250	1638	91.8	29250	1437	92.7
	Method 25				-f-	4352	77.2
Condition 2[e]:	GC/FID[b]				32270	484	97.3
	FID[c,d]	29390	356	98.2	29390	320	98.3
	Method 25				-f-	1148	94.4
Plant B							
Condition 1:	GC/FID[b]				32890	540	96.3
	FID[c,d]	31050	392	97.0	29990	285	97.8
	Method 25				24670	530	95.0
Condition 2[e]:	GC/FID[b]				35470	2	99.9
	FID[c,d]	30540	29.7	99.7	29380	29	99.6
	Method 25				24240	269	97.1

[a] Percent efficiency calculated from mass emission (g/sec) values.

[b] Integrated bag sample, peak summation less methane.

[c] Integrated bag sample, direct FID measurement (column bypass).

[d] GC methane value subtracted to calculate non-methane value.

[e] Increased incineration temperature.

[f] Inlet not sampled by Method 25; percent efficiency calculated using GC/FID non-methane value for inlet concentration.

yielded efficiency results only slightly less than GC, in two cases the outlet concentration measured by EPA 25 was significantly higher than those measured by GC (Condition 2, Plants A and B). The higher (in one case, 100 times) emission data at the outlet do not significantly affect the calculated control device efficiencies because the inlet concentration is quite high (30,000 ppm); consequently, outlet measurements of 3 ppm and 300 ppm result in efficiencies of 99.9 and 99.0 percent, respectively. In a situation of lower inlet concentration (1000 ppm range, for example) the higher results obtained by EPA 25 at the outlet could significantly affect the calculated control device efficiency. The phenomenon of high (relative to GC or FID) EPA 25 result has been experienced at other test locations and appears to occur particularly as the outlet concentration decreases below the 100 ppm level. It is believed that this phenomenon is related to contamination in the sampling equipment and/or analytical system. EPA is currently investigating the possible causes of this problem and is looking at appropriate solutions (e.g., increased laboratory quality assurance and larger sample volumes). One other point related to the test data warrants mention. EPA 25 data at the Plant B inlet (no EPA 25 data were obtained at the Plant A inlet) are consistently about 20 percent lower than the GC or FID data. Based on recent results of a laboratory study conducted by MRI[3], it is believed that these low results are due to the presence of highly polar compounds in the inlet stream. It is suspected that the GC column currently specified in EPA 25, although adequate for the compounds (solvents) normally used in the surface coating industries, is not adequate for analysis of some of the polar compounds found in the air oxidation process effluent. Further work is planned in this area to determine if the EPA 25 GC column is indeed the problem, and, if so, how it may be improved.

D.2.2 Recommended Test Method

The CG/FID is the recommended test procedure for determining control device efficiency for air oxidation processes. A general GC procedure is discussed in the OAQPS publication, "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography,"[4] presented as Attachment I to this appendix.

Method 25 can be used as an alternative procedure, but is likely to yield slightly lower calculated efficiencies. Method 25 can be expected to yield higher results than the GC method at the emission outlet when the outlet concentration is less than 100 ppm, volume, therefore, at this time, Method 25 is particularly not recommended for performance tests to measure compliance with the 98 percent or 20 ppm VOC reduction provision of the proposed standard when the outlet emissions are expected to be below this level.

D.3 MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

In order to determine the volume percent VOC concentration and stream net heating value for air oxidation sources, both identification and quantification of the substances being emitted are necessary. The generalized gas chromatography method described in Attachment I to this appendix can be used to (1) determine hourly VOC emissions from the control device outlet, (2) determine VOC reduction efficiency of the control device, and (3) provide data required to determine whether a source has a TRE index value above or below the cutoff level specified in the proposed standard.

D.4 DETERMINATION OF NET HEATING VALUE AND VOC EMISSION RATE OF EXHAUST GAS STREAMS

These methods describe the calculation of the net heating value and VOC emission rate of gas samples. They specify methods the organic compound content, carbon monoxide content, hydrogen content, and moisture content of the gas sample. These compositional data are used along with published or measured values for the net heats of combustion and molecular weights to calculate the heating value and VOC emission rate of the gas sample. The complete methods for heating value and VOC emission rate determination determination are included as Attachment II to this appendix.

D.5 REFERENCES FOR APPENDIX D

1. Emission Test Report: Union Carbide Corporation; Taft, Louisiana. OAQPS, Emission Measurement Branch Report No. 78-OCM-8, September 1980.

2. Emission Test Report: Rohm and Haas Company; Deer Park, Texas. OAQPS, Emission Measurement Branch Report No. 78-OCM-9, August 1980.

3. Evaluation of Method 25 for Air Oxidation Processes. Midwest Research Institute, Contract No. 68-02-2814, Task 36 (report not yet available).

4. Measurement of Gaseous Organic Compound Emissions by Gas Chromatography. OAQPS, Emission Measurement Branch.

ATTACHMENT I TO APPENDIX D: MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

DISCLAIMER

Mention of trade names or specific products in this method does not constitute endorsement by the Environmental Protection Agency.

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SECTION 1

INTRODUCTION

1.1 PURPOSE

Characterizing emissions from industrial sources requires both identification and quantification of the substances being emitted. This method provides a methodology for sampling and analyzing gaseous organic emissions from stationary industrial sources to verify the existence of compounds thought to be present and to quantify their emission levels.

The procedures described in this manual are intended to be used by persons skilled in planning and executing sampling efforts using *Federal Register* methods. Enough background information is provided so that such persons can: (1) characterize the organic gaseous emissions using gas chromatography/flame ionization detector (GC/FID), (2) verify the operation of the instrumentation and collection devices by means of audit samples and quality control procedures, and (3) report the results in terms of the concentration of major pollutants from the source.

Subsequent sections of this method discuss various aspects of the sampling system, conditions that may be encountered in source sampling, and options that must be considered to analyze gaseous organics successfully.

1.2 SOURCE TYPES AND EXPECTED SAMPLING CONDITIONS

Although organic chemical production involves many different types of raw materials, processes, and products, many of the unit operations are the same, e.g., distillation columns, dryers, scrubbers, and mixing equipment. The expected gaseous emissions, temperatures, velocities, pressures, and humidities from these operations are given in Table 1.

Temperatures in organic emission sources normally range from ambient to 300°C (570°F). Paint spray booths and similar hood-type operations operate at or above the plant ambient temperatures. Operations that involve heating have emissions at 400°C (700°F). Sources with higher temperatures typically emit gases of low molecular weight (CO, CO_2, H_2O, CH_4, etc.) because of thermal decomposition of all but the most thermally stable organic compounds. Flare stacks and most high-temperature incinerators fall into this latter category. (Organic analysis for incinerator emissions generally involves particulate and high-molecular-weight organic vapors, such as polycyclic organic materials (POM's) and other less volatile compounds.)

As seen in Table 1, the amount of moisture present in organic emissions varies over a wide range. The effluent from vents, tanks, or similar process lines may contain little or

Table 1. CHARACTERISTICS OF POTENTIAL ORGANIC EMISSION SOURCES

Potential organic emission sources	Composition Part.	NO_x	SO_x	CO	HC	Relative humidity, %	Acid content	Temperature °F	Pressure, psig	Flow rate, scfm
Storage tanks					x	0-20	x	-54 - 300	0-2	<100
Unloading facilities					x	0-20	x	-54 - 200	0-2	<100
Chemical reactors										
Non-catalytic				x	x	0-20	x	-20 - 1000	0-1500	100-10,000
Catalytic										
Fluidized bed	x			x	x	0-20	x	0 - 300	0-50	100-10,000
Fixed bed	x			x	x	0-20	x	0 - 300	0-50	100-10,000
Moving bed	x			x	x	0-20	x	0 - 300	0-50	100-10,000
Distillation column				x	x	0-98	x	80 - 250	0-50	100-10,000
Flash separator				x	x	0-98	x	-48 - 300	0-50	100-10,000
Filters										
Pressure leaf filters	x				x	0-98	x	70 - 150	0-10	100-10,000
Rotary vacuum filters	x				x	0-98	x	70 - 150	0-20	100-10,000
Nutsche filters	x				x	0-98	x	70 - 150	0-10	100-10,000
Horizontal plate filters	x				x	0-98	x	70 - 150	0-10	100-10,000
Tubular filters	x				x	0-98	x	70 - 150	0-10	100-10,000
Bag filters	x	x	x	x	x	0-98	x	70 - 150	0-10	100-10,000
Mixers					x	0-20		32 - 90	0-2	100-10,000
Grinders	x				x	0-20		32 - 90	0-2	100-10,000

Table 1. CHARACTERISTICS OF POTENTIAL ORGANIC EMISSION SOURCES (Continued)

Potential organic emission sources	Composition					Relative humidity, %	Acid content	Temperature ^oF	Pressure, psig	Flow rate, scfm
	Part.	NO_x	SO_x	CO	HC					
Crushers	x				x	0-20		32 - 90	0-2	100-10,000
Scrubbers		x	x	x	x	80-95	x	60 - 150	0-10	>10,000
Dryers										
Counter-current dryer	x	x	x	x	x	0-95	x	100 - 300	0-20	100-10,000
Rotary drum dryer	x	x	x	x	x	0-95	x	100 - 300	0-20	100-10,000
Vacuum rotary dryer	x	x	x	x	x	0-95	x	100 - 300	0-35	100-10,000
Spray dryers					x	0-95	x	100 - 300	0-20	100-10,000
Screeners	x				x	0-20		32 - 100	0-2	100-10,000
Waste incinerators	x	x	x	x	x	40-95	x	500 - 1500	0-5	>10,000
Utility boilers	x	x	x	x	x	40-95		500 - 1500	0-5	>10,000
Pneumatic conveyors	x				x	10-30	x	40 - 90	0-20	>10,000
Conveyor belts	x				x	0-20		32 - 90	0-2	<100
Extruders		x	x	x	x	0-20		100 - 350	0-2	<100
Pellitizers					x	0-20		100 - 200	0-2	<100
Paint spray booths	x				x	0-20		60 - 100	0-5	>10,000
Ovens	x	x	x	x	x	0-50		500 - 1500	0-2	>10,000
Blenders	x				x	0-20		32 - 90	0-2	100-10,000
Cyclones	x				x	0-20		70 - 150	0-20	10,000
Extraction towers					x	0-90	x	70 - 300	0-50	100-10,000

Table 1. CHARACTERISTICS OF POTENTIAL ORGANIC EMISSION SOURCES
(Continued)

Potential organic emission sources	Composition					Relative humidity, %	Acid content	Temperature ^oF	Pressure, psig	Flow rate, scfm
	Part.	NO_x	SO_x	CO	HC					
Flares	x	x	x	x	x	40-95		1500 - 3000	0-2	>10,000
Baggers	x				x	0-20		100 - 200	0-2	<100
Loading facilities	x				x	0-20	x	-54 - 300	0-2	<100
Cooling towers					x	40-95		32 - 100	0-2	100-10,000
Settling ponds					x	40-95	x	32 - 80	0-2	100-10,000
Evaporators					x	0-95	x	100 - 200	0-50	100-10,000
Leaching vat					x	0-95	x	100 - 200	0-2	100-10,000
Cookers	x	x	x	x	x	0-95	x	100 - 300	0-2	100-10,000
Refrigeration machines						0-10		-50 - 32	50-300	<100

Snyder, A.D., F.N. Hodgson, M.A. Kemmer, and J.R. McKendree. Utility of Solid Sorbents for Sampling Organic Emissions from Stationary Sources. EPA 600/2-76-201, U.S. Environmental Protection Agency. Research Triangle Park, N.C. July 1976. 71 pp.

no moisture or may be saturated with water vapor. The selected procedures for sampling must normally prevent the condensation of water in order to avoid the generation of unrepresentative samples. However, if the organics of interest are water misicible, then collection in water-filled impingers may be satisfactory.

Pressures encountered in organic sources are important because: (1) the sampling system must be able to withstand the expected source pressures and (2) the source pressure defines the pumping requirements of the sampling system. Typically, gauge pressures range from slightly negative to several pounds per square inch positive.

CO, NO_x, SO_x, and particulate compositions are presented in Table 1 because they are potential interferents. Because some acid gases vary the structure of some organic compounds and cause false data, the components of the sampling system must be made of corrosion-resistant materials. Particulates in the source gases must be selectively excluded from the sampling train for two reasons: (1) the surface of the particulates may adsorb organic components and (2) high particulate levels can clog portions of the gas sampling system and the chromatograph.

The concentrations of organic components in the source effluent can vary between 10 and several thousand ppm. At the lower end of the concentration range the FID sensitivity is quite adequate. At the higher concentration levels, however, dilution of the source gases may be required.

1.3 SAMPLING PROCEDURES

Techniques used to collect samples for organic analysis include: adsorption tube sampling, instantaneous flask sampling, integrated bag sampling, integrated solvent sampling, porous polymer collection and concentration, and direct interfacing. These methods are described below, and their advantages and disadvantages are discussed.

1.3.1 Adsorption Tube Sampling

In this procedure, volatile organic vapors are collected on suitable adsorption media contained in glass tubes. The method closely follows volatile organic methods contained in the NIOSH Analytical Methods series. Desorption recovery efficiency must be determined for the organic species present and must be at least 50 percent.

1.3.2 Instantaneous Flask Sampling

Instantaneous grab sampling, as the name implies, consists of collecting a sample in glass sample bulbs, cylinders, or syringes in a few seconds. If repeated on a frequent schedule, this technique can indicate short-time variations in the emission concentrations.

The source is sampled in one of two ways. The first way is to evacuate the cylinder to low pressures typical of a good quality vacuum pump and to connect it to a sample probe and a tee connector. One leg of the tee is connected to a mercury manometer; the other leg is used to purge the sample line with source gas using a rubber suction bulb. Then the stopcock in the cylinder is opened to admit a sample. The procedure is very similar to EPA Method 7 for withdrawing NO_x samples.

The second approach is to use a flow-through system. The source gas is drawn through the sampling cylinder by a pump or rubber suction bulb until the gas has been purged from the cylinder three or four times. After the cylinder has been purged, the stopcocks are closed to contain the gas for analysis.

There are several problems associated with this technique. If the sample gas is hot during the collection operation, condensation and adsorption will most likely occur as the gas cools to ambient temperature; therefore, the container should be heated before analysis. If pressure is not a problem, the container should be heated before analysis to 10-20°C above the source temperature to revaporize the condensed organic compounds.

Another problem involves the cleaning of sampling vessels. For a glass vessel, organic contamination can be removed from the interior by heating at a temperature just below the annealing point of the glass. This treatment is generally sufficient to remove any condensed or adsorbed materials, but it will not remove those that can chemically bond to glass. After heating, the vessel is cooled under a flowing stream of inert gas (high-purity nitrogen or helium), which is retained in the flask after cooling. Background data are obtained ay analyzing this gas by GC/FID or

GC/mass spectrometric (GC/MS) methods. The least complicated approach is to use a FID without a GC column to obtain a relative measure of total organic content. The GC/MS method, if used, would identify any contamination and indicate its origin.

1.3.3 Integrated Bag Sampling

Integrated bag sampling provides time-averaged samples. The sampling may, therefore, be designed to represent average source conditions over given time periods, such as complete cycles of a batch operation.

In this approach the sample is withdrawn from the source into an inert bag through an optional cooling condenser and a leak-free pump (see Figure 1). One problem with this technique occurs when condensation takes place, in which case the condensate must be analyzed. A second problem is the procurement of a satisfactory leak-free, corrosion-resistant and organic-contaminant-free pump.

A better arrangement is shown by the dotted line portion of Figure 1. The gas is filtered by an in-stack glass wool plug in the probe system to minimize condensation of water and organic compounds. The gas is then directed from the probe into a plastic bag by evacuating the airtight chamber around the bag. As a result, the sample is not contaminated by passage through needle valves, flow meters, or the pump. This arrangement has been used on paint spray booths and bake ovens to sample individual stacks and, by using a manifold system, to sample several stacks simultaneously.

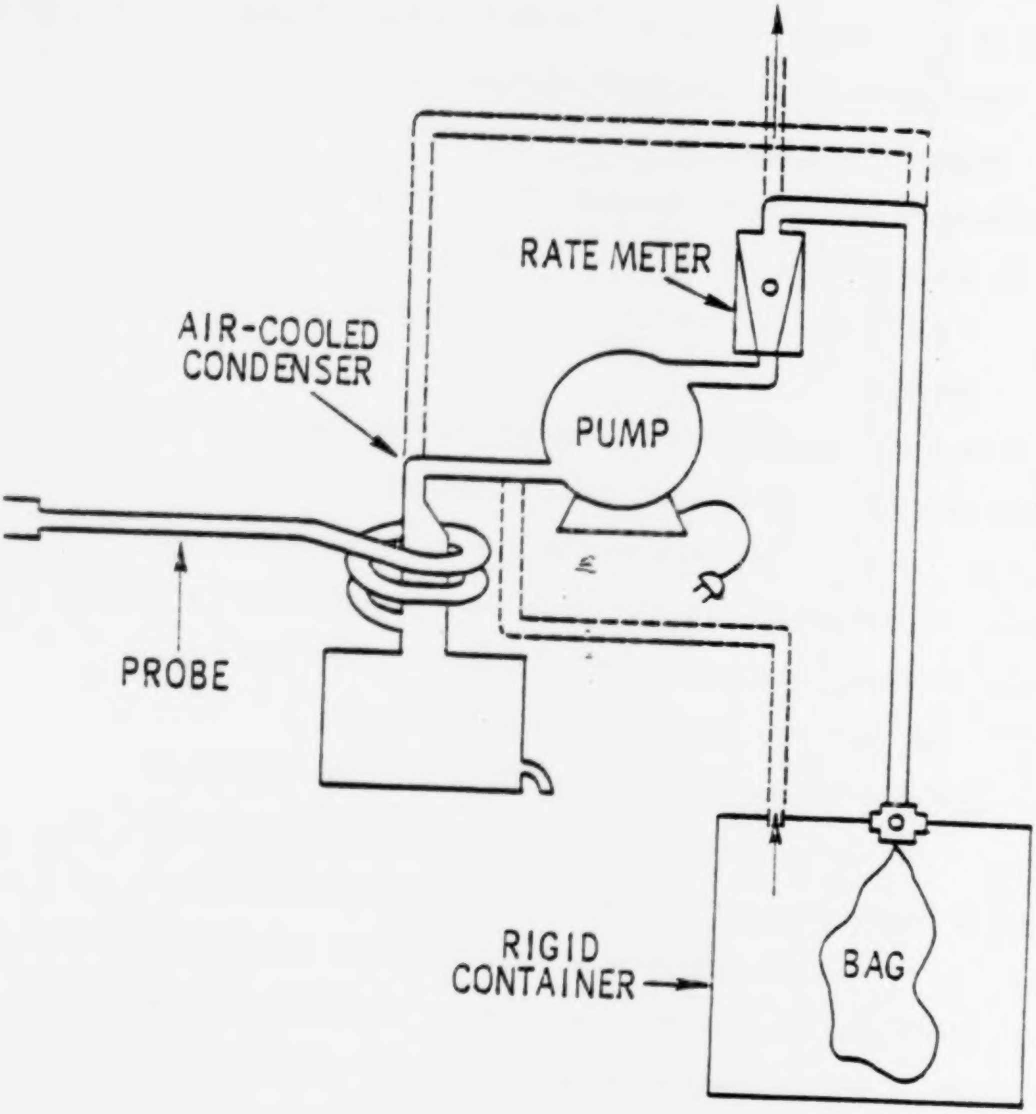
RATE METER
AIR-COOLED CONDENSER
PUMP
PROBE
RIGID CONTAINER
BAG

Figure 1. Integrated gas sampling train. Solid lines indicate normal arrangements. Dotted lines show alternate arrangement with evacuating chamber around bag.

The same arrangement is used in Method 106 for sampling vinyl chloride in stationary sources.

If condensation occurs, the problem may be overcome by heating the bag containing the sample to source temperature prior to analysis, or by maintaining the temperature at source levels during collection, transport, and analysis. Dilution of the gas in the bag could also solve the condensation problem, and, in addition, reduce highly concentrated gas streams to a measurable level.

The source gas can be diluted prior to collection in the bag by metering both the gas and charcoal-cleaned ambient air (or clean inert gas) through calibrated flow meters with micrometer valves. A dilution ratio between 5:1 and 30:1 would be used, depending on the concentrations required by the analytical instrument. An alternative method for diluting the source gas would be to prefill the bag partially with a known quantity of inert gas and then meter in a known quantity of the source gas.

The choice of a bag material is an important consideration. Possibly acceptable bag materials are Tedlar,[1] Teflon, and aluminized Mylar. Mylar, polyethylene, or Saran bags suffer from reduced recovery of known concentrations of sample gases. Tedlar provides slightly better recovery than Teflon, but over short time periods the difference is not significant. The actual recovery of samples collected in the Tedlar or Teflon bags depends on the nature of the organic emissions. The higher the source temperature and the more polar the organic compounds being studied, the greater the losses of material observed during storage periods up to several days. Most of the loss appears to occur in the first few minutes. After this initial period, the loss rate is relatively small over the next several days.

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[1] Mention of trade names or specific products does not consitute endorsement by the U.S. Environmental Protection Agency.

Reusing Tedlar or Teflon bags can also cause some problems. In one case, a Teflon bag had been used to collect samples of source gas containing cumene (isopropyl benzene) at a level of about 1100 ppm. After the analysis was completed, this bag was flushed with nitrogen and evacuated three times. After the third evacuation, the bag was filled with nitrogen and analyzed. The analysis indicated less than 0.01 ppm of cumene. One week later, the gas was analyzed again and 64 ppm of cumene was found. This indicates very clearly that this material is absorbed into the bag and diffuses very slowly from the plastic material. Since this effect could be fairly common, it is strongly suggested that new sample bags be used whenever possible, and that they definitely be used when samples are to be stored more than an hour or two.

Since the loss of material in the bag depends on several factors (temperature, concentration, and polarity of the material), the amount of loss to be expected will vary greatly from site to site. Known standards of the components in a pseudo-stack gas can be prepared at several concentration levels and collected in a bag identical to the one to be used for the source sampling. The contents of this bag may then be used to calibrate the GC instruments or, if other calibration gases are available, to evaluate the sample recovery efficiency.

1.3.4 Integrated Solvent Sampling

If the organic emissions are water misicible, then sampling with water-filled impingers may be a feasible approach. Other solvents might also be used.

1.3.5 Porous Polymers

Organic vapors and hydrocarbons are frequently trapped on a porous polymer compound substrate such as Tenax GC, XAD-2, Chromosorb Century Series, or Porapak resins. This approach is useful for concentrating trace amounts of organic compounds and for materials of molecular weights of C_6 and greater. It is being employed in the collection of high molecular weight organic compounds (POM's) and in source assessment sampling systems. The major problem is that low molecular weight compounds are not efficiently collected, and therefore it would be necessary to carry out collection and desorption efficiency studies on many of the compounds of interest. Another problem results when some of the porous polymer organic resins react with certain oxidants (i.e., NO_2, inorganic acids, etc.). These resins decompose and yield organic materials that will contaminate the sample.

There may be several advantages to porous polymers in certain situations. First, the polymers do not tend to trap water, and so it is possible to collect the organic compounds and let the water vapor pass through. Second, collected samples are easy to transport. Third, the container can be capped and then stored at 0°C until analyzed. In the closed and cooled condition, the tubes can be held several weeks prior to analysis. The adsorbed compounds can be removed from the tube either by heating it while passing an inert gas (usually the GC carrier gas) through it, or by passing a suitable solvent through the tube. Solvent desorption, if a suitable solvent is found, provides sufficient material for several analyses on the same sample, whereas the thermal desorption is a one-time approach.

However, the porous polymer approach is not suggested for routine sampling because of the loss of low-molecular-weight compounds, which are of major interest, and because of the lack of a need to concentrate the sample to reach the desired detection limits. In certain situations and when collection efficiency data are available, porous polymer collection may be a viable option.

1.3.6 Direct Coupling and Interfacing

The most accurate method for sampling and analysis is to couple the gas chromatograph directly to the source. Its use depends on the similarity of the source gas (temperature, pressure, composition) to the requirements of the gas sampling system of the GC instrument.

The problems to be considered are the materials of construction, the presence of particlate and water vapor, the temperatures of the gases and of the sample valving system of the GC, the concentration of the gaseous organic species in the gas stream, and the accessibility of the location of the stack vent being sampled.

The presence of particulate in the source gas can present a severe problem for the GC operation. The simplest solution is to use an in-stack filter with an enlarged probe at the gas inlet end and a plug of glass wool inserted in this enlarged area. The probe itself can be made of 0.25-inch stainless steel tubing, and connectors can be used to enlarge the diameter of the probe to accommodate 0.5-inch tubing to contain the glass wool filter. Since the filter can be in the stack, it can in a short time reach the stack temperature, and condensation of water and organic compounds can be minimized. The filter should be replaced each time a new site is sampled.

The problem of water vapor condensation is not so simply solved. Water dissolves polar organic compounds, and large quantities restrict the flow in the sample lines.

To prevent condensation, (1) the sample lines may be heat-traced to maintain the sample gas temperature above the dew point or at stack temperature, or (2) the source gases may be diluted as close to the source as possible. The choice depends on the source temperature and the concentration of the organic compounds in the source. If the concentration of organic compounds is so high that the FID will be saturated, the obvious answer is to dilute the source gas.

The sample gas can also be dried, or the water can deliberately be condensed. Procedures for determining low-molecular-weight hydrocarbons sometimes include the use of condensers held at 0°C to remove water, and drying agents such as Ascarite or silica gel. These methods are useful in those situations where in the emissions of interest are low-molecular-weight (C_1 to C_5) alkanes and alkenes. They are not applicable, however, for polar compounds and materials with low vapor pressures at 0°C unless the condensate can be analyzed. This approach obviously could not be used on all source emissions.

The major restraints on the design of the interface are the source gas and GC temperatures. The sample lines from the probe to the instrument must be heat-traced with electrical resistance heating. The probe should contain a Type K thermocouple for monitoring and/or regulating the temperature. The temperature of the source gases should also be monitored with a second Type K thermocouple attached to the outside of the probe. The sample lines should be as short as possible, consistent with the physical requirements of the site. A diagram of the apparatus is shown in Figure 2.

Situations will likely occur in which the source gas must be diluted because of the higher source temperature, water vapor, and/or high organic compound concentrations. This dilution should be performed with inert gas or charcoal-cleaned ambient air. It can

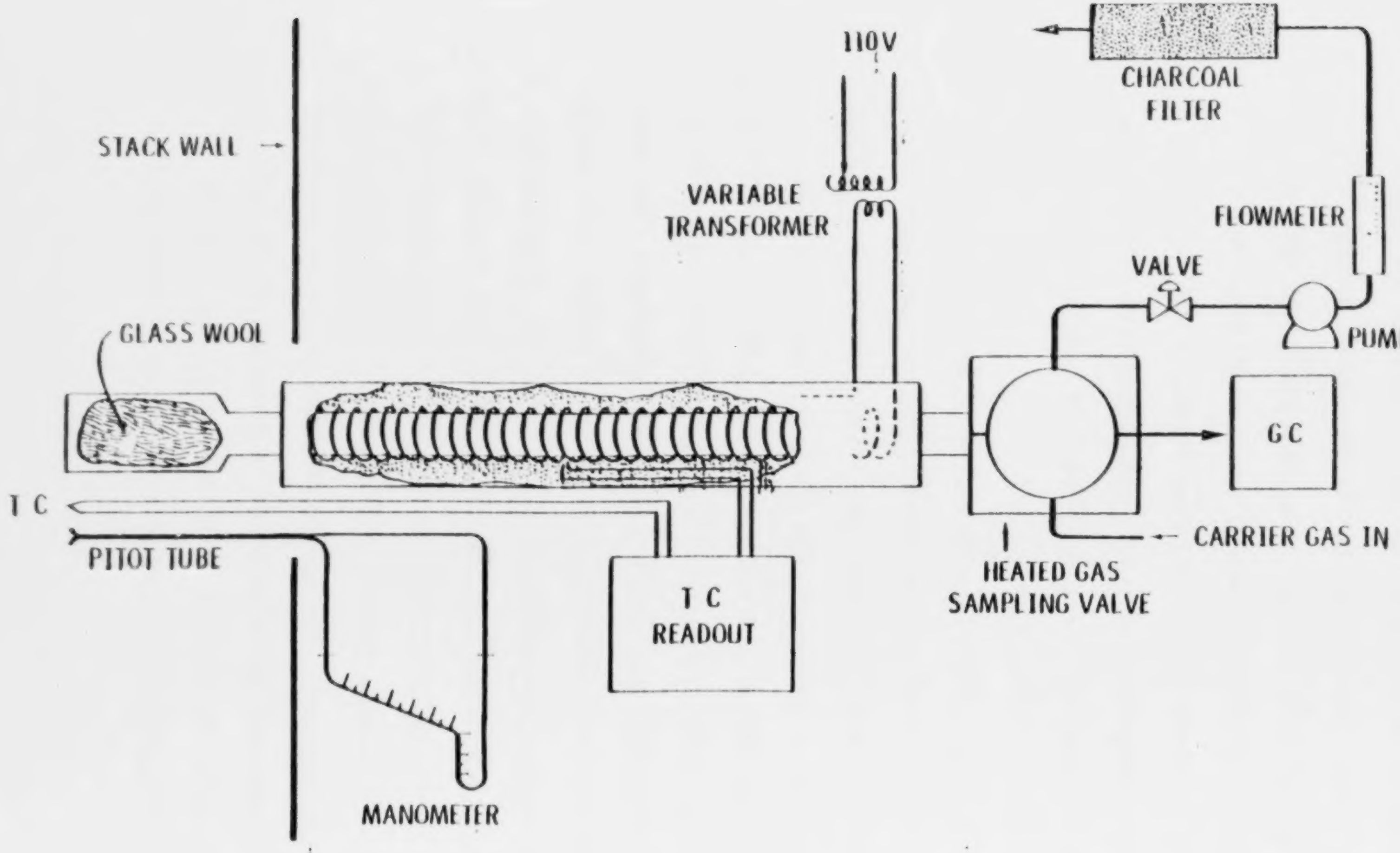

110V
CHARCOAL FILTER
STACK WALL
VARIABLE TRANSFORMER
FLOWMETER
VALVE
GLASS WOOL
PUMP
GC
T C
PITOT TUBE
CARRIER GAS IN
HEATED GAS SAMPLING VALVE
T C READOUT
MANOMETER

Figure 2. Sampling system for analysis of undiluted source gas.

be accomplished by installing a tee fitting between the sample line and the probe. The diluent gas is then added through this tee. The flows of both the stack gas and diluent gas must be measured with calibrated flow-meters and micrometer valves to determine the dilution ratio. Dilution ratios in the range of 1:5 to 1:30 are desirable. For this approach a larger-than-normal pumping rate is required in the sampling line, with the rate varying with the required dilution factor.

The calibration of the GC with either interface system will depend on the substitution of calibration gas for the source gas. A Tedlar bag containing a standard gas mixture should be connected to the filter end of the probe, and the same pumping rate and dilution used for source gas should be used to obtain the calibration data. Ideally, the flow rates and gas sampling pressures will be identical. This will make accurate calibration of each flow meter and gas sampling valve unnecessary since these factors will cancel. The standard gas concentrations are used to prepare a calibration curve, and the source gas concentrations can be read directly from the curve. During sampling, corrections will have to be made for the pressure differences between the standard mixtures (atmospheric) and the source pressure. The source pressure is easily determined with a pitot tube and manometer prior to the start of the test. For the most part, the sources to be tested will be close to atmospheric pressure, varying by several inches of water plus or minus; and this pressure difference will have little effect on the results. This will not be true for process gas streams, and pressure corrections must be made or the sample must be collected by one of the methods discussed in Sections 1.3.2, 1.3.3, or 1.3.4.

1.4 REVIEW OF ANALYTICAL TECHNIQUES

1.4.1 Instrument Design Considerations

The analytical instrumentation must be designed to withstand field use. The gas chromatograph must be capable of producing accurate data, but a fully equipped research-quality instrument is not normally required. The instrument must be rugged enough that it will not be rendered inoperable by transportation from one sampling site to another. It must afford good temperature control for the analytical column, the injection port, the gas sampling valve, the sample loop, and the detector. The gas sampling system must provide reproducible injections into the chromatograph and maintain the integrity of the sample from the stack to the detector. Temperature programming is a desirable option in view of the wide variety of compounds likely to be encountered. An intrinsically safe (explosion proof) chromatograph is a definite asset to the program. In some situations, constant-voltage or constant-phase transformers may be required in the line prior to the electronics for the FID and the electrometer.

1.4.1.1 Portable Gas Chromatographs

These commercially available instruments are completely self-contained. Rechargeable lecture-bottle-size cylinders contain the necessary gases, and rechargeable nickel-cadmium batteries supply the power. They do not require large gas cylinders or electrical service.

However, these portable chromatographs do have certain disadvantages. Typically, more time is required for temperature equilibration than with nonportable instruments. In addition, the supply of the gases in the small cylinders limits the length of time the instrument may be used for actual analysis. Since these cylinders must be periodically recharged, large cylinders may still be necessary when one sampling trip is to cover several plants in different cities before returning to a "home base." The most severe problem with portable instruments is that most are not temperature programmable.

1.4.1.2 Laboratory Gas Chromatographs

For the above reasons, the use of a temperature-programmable laboratory chromatograph is advisable; but an extremely sensitive, research quality instrument replete with accessories and options such as automatic oven door openers, subambient capability, and multiple detectors is not necessary. However, a certain degree of durability is necessary to withstand transport. The major disadvantages of a laboratory chromatograph are the handling of the necessary gases and the availability of electrical power in the field.

1.4.2 Gas Chromatographic Column Selection

Information pertinent to column selection must be available prior to actual field analysis. Background information is generally available for various processes, including typical components of the stack gases for a given process, the approximate concentration levels of these components, and information regarding temperatures and flow rates of the stack gases. This information is quite helpful in selecting not only the proper column or columns, but also GC operating conditions such as column temperature, injection port temperature, flow rates, etc. Analysis of a sample that is collected during a pretest site survey provides the only reliable information regarding compounds present, approximate levels, quantity of water vapor present, etc., upon which decisions can be based concerning column type, predilution, and GC conditions. When the organic portion of the stack emissions contains compounds with widely varying molecular weights and volatilities, multiple columns must be used.

The types of columns from which final selections can be made include: (1) the Porapak series, (2) one of the Chromosorb Century series, and (3) Carbosieve B for the low-molecular-weight, highly volatile compounds, and (4) Tenax GC or one of the Dexsils for the higher-molecular-weight compounds. A summary of some of the column materials, their properties, and their usefulness is given in Supplement I-A.

1.4.2.1 Multiple Columns

When no single column can provide efficient separation of a complex mixture of compounds having widely varying molecular weights and boiling points, multiple columns may be employed. Using either two individual GC units, each possessing a different column, or one GC with a change of columns is expensive and time consuming. Two or more columns in a single GC operation is more advantageous. For the latter, the most convenient method requires each of the two individual column outlets to enter separate detector cells. However, if the GC unit is not equipped with or cannot be modified to accommodate this type of ancillary equipment, two or more columns may be connected either in series or in parallel. When multiple columns are connected in series, the sample enters each column successively; when parallel connection is used, the sample and carrier gas stream is split into individual fractions, and one portion of the sample enters each column.

1.4.2.2 Preconditioning Columns

Every new GC column requires conditioning prior to its initial use. Conditioning is ordinarily achieved by heating the packed column in a stream of carrier gas to the maximum operating temperature anticipated for a period of time ranging from a few hours to a few days, depending on the column materials chosen. To avoid contaminating the detector, the column outlet should not be connected to it until the final stages of conditioning. When a stable baseline is achieved, conditioning can be assumed to be essentially complete.

Conditioning the column removes volatile impurities, water, and any solvent remaining from the deposition of the liquid phase on the support and provides a more uniform distribution of liquid phase on the solid support. In addition, conditioning serves to activate (or, in the case of some special-purpose stationary phases, to deactivate) the solid stationary phase.

1.4.3 Data Presentation

1.4.3.1 Recorder Options

Desirable features on both portable and laboratory recorders include multiple voltage range (1 millivolt to 1 volt), variable chart speed, a reliable pen assembly, and a chart width adequate for accurate peak determination. The recorder must remain fairly stable, must not drift excessively, and must not contribute significantly to the "noise" transferred to the pen.

1.4.3.2 Peak Integration

An excellent alternative to the typical recorder is an integrator. The integrator obviates calculations of the peak heights or peak height times width at half the peak height. An integrator such as the Hewlett-Packard Model 3380A not only provides a traced chromatogram, as does a conventional recorder, but it also provides a display of the retention time of the components or absolute quantity calculations based on programmed internal or external standards. The integrators greatly facilitate GC analyses, including those performed in the field.

1.5 SAFETY CONSIDERATIONS

The tester must be aware of all existing and potential hazards with respect to emission testing and comply with existing OSHA and specific plant requirements. Although the dangers associated with source sampling are well known to anyone who has been active in this area, there are some unique features of organic vapor sampling that should be considered.

Cylinders of hydrogen, air, and helium (or nitrogen) are required for the operation of the chromatograph. All connections should be leak checked using soap solution or one of the commercial leak-check solutions. Cylinders of these gases should not be transported in a closed vehicle. The safest approach is to ship all cylinders of the gases to the sampling site by suitable commercial carriers.

Before samples are collected, sampling lines must be purged in a manner that will eliminate exposure of any personnel to the gases. All gases should be assumed to be toxic. Similarly, the gas used to flush the sampling loop and any gas evacuated from sampling bags should be trapped to prevent personnel exposure. Charcoal tubes can be used for this purpose.

Audit samples of the source gas components required to verify the analysis procedures will contain gases with concentrations between 10 and 10,000 ppm. These gas samples should also be treated as if they were extremely toxic to avoid exposure of any person handling them.

Electrical power supply sources should be checked prior to use to be sure receptacles have been wired to code specifications. Circuit checkers are commercially available for this purpose.

The test team must be aware of plant restrictions regarding flame detectors, locations of safety showers, eye wash fountains, first aid stations and medical help, evacuation alarms, and paths of egress. Each tester must also be equipped with the required personal safety equipment (hard hats, safety glasses, ear protection, respirators or air packs, safety shoes, etc.). Safety indoctrinations are required at many plant sites before work can begin; and even at those locations where safety checkouts are not formally required, they should be considered as essential for the test team. The safety aspects must not be compromised for any reason.

SECTION 2

DETAILS OF THE METHOD

2.1 APPLICABILITY AND PRINCIPLE

This method provides concentration data on approximately 90 percent of the total gaseous organic mass emitted from an industrial source. It does not include techniques to identify and measure trace amounts of organic compounds, such as those found in building air and fugitive air emission sources.

This method is based on separating the components of a gas mixture in a gas chromatographic (GC) column and measuring the separated components with a flame ionization detector (FID). This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize (such as formaldehyde), (3) have very low vapor pressures at stack or instrument conditions or (4) exhibit poor response with the FID.

The method also depends on comparing the retention times of each separated component with those of known compounds under identical conditions. Therefore, the analyst must suspect the identity and approximate concentration of the organic emission components beforehand. With this information, the analyst can prepare standard mixtures to calibrate the GC under conditions identical to those that the samples will exhibit. The analyst can also determine the need for sample dilution to avoid FID saturation, gas stream filtration to eliminate particulate matter, and moisture condensation prevention. This method cannot be applied without this prior information.

2.1.1 Range of Applicability

The sensitivity of this method is about 10 parts per billion. The upper end is limited by detector saturation or column overloading. It can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

2.1.2 Precision and Accuracy

GC techniques typically provide a precision of ± 5 to 10 percent relative standard deviation (RSD), but an experienced GC operator and a reliable GC/FID instrument can readily achieve a ± 5 percent RSD. For this method, the following combined GC/operator values shall be met:

(1) Repeatability. Duplicate results by the same operator will be rejected if they differ by more than ± 5 percent.

(2) Accuracy. The results of prepared audit sample analyses will be considered deficient if they differ by more than ± 10 percent from the preparation values.

The accuracy of the sampling and analytical procedure on stack gases cannot be defined since the actual emission values are not known. However, the accuracy and the validity of the sampling and analysis will be evaluated by using both on-site calibration with known mixtures and prepared audit samples.

Based on the precision and accuracy of the GC method, analysis of industrial sources is estimated to be within ± 10 percent of the actual values.

2.2 PRESURVEY OF SOURCE

The purpose of the presurvey is to obtain all information necessary to design the emission test. The most important presurvey data are the average stack temperature and temperature range, approximate particulate concentration, static pressure, water vapor content, and identity and expected concentration of each organic compound to be analyzed. Some of this information can be obtained from literature surveys, direct knowledge, or plant personnel. However, grab samples of the gas must be obtained for analysis to confirm the identity and approximate concentrations of the specific compounds. A moisture determination should also be made. A suggested presurvey form is given in Figure 3.

2.2.1 Collection of Grab Samples - Glass Sampling Flasks

Grab samples can be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks having glass stopcocks with grease should be cleaned as follows.

Remove the stopcocks from both ends of the flask, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with chloroform. Clean all glass ports with Micro Cleaning Solution, then rinse with tap and distilled water. Place the flask in a cool glass annealing furnace and apply heat up to 550°C. Maintain at this temperature for 1 hour. After this time period, shut off and open the furnace to allow the flask to cool. Grease the stopcocks with Spectavac grease and return them to the flask receivers.

PRELIMINARY SURVEY DATA SHEETS
GASEOUS ORGANIC ANALYSIS-GC METHOD

I. Name of Company ______________________________ Date __________

Address ______________________________

____

Contacts ______________________________ Phone __________

______________________________ __________

Process to be Sampled ______________________________

____

____

Duct or Vent to be Sampled ______________________________

____

II. Process Description ______________________________

____

____

____

____

Raw Material ______________________________

____

____

Products ______________________________

____

____

Operating Cycle

Check: Batch ________ Continuous ________ Cyclic ________

Timing of Batch or Cycle ______________________________

Best Time to Test ______________________________

Figure 3. Preliminary survey data sheet.

PRELIMINARY SURVEY DATA SHEETS
GASEOUS ORGANIC ANALYSIS-GC METHOD

III. Sampling Site

A. Description

Site Description ______________________________

Duct Shape and Size ______________________________

Material ______________________________

Wall Thickness ______________________________ inches

Upstream Distance __________ inches __________ diameter

Downstream Distance __________ inches __________ diameter

Size of Port ______________________________

Size of Access Area ______________________________

Hazards ____________________ Ambient Temp. ______ °F

B. Properties of Gas Stream

Temperature _____ °C _____ °F, Data Source __________

Velocity ______________, Data Source __________

Static Pressure ___ inches H_2O, Data Source __________

Moisture Content __________ %, Data Source __________

Particulate Content __________, Data Source __________

Gaseous Components

N_2 ________ %		Hydrocarbons	______ ppm
O_2 ________ %		________	______
CO ________ %		________	______
CO_2 ________ %		________	______
SO_2 ________ %		________	______

Hydrocarbon Components

____________	________ ppm
____________	________ ppm
____________	________ ppm
____________	________ ppm
____________	________ ppm
____________	________ ppm

Figure 3(Continued). Preliminary survey data sheet.

PRELIMINARY SURVEY DATA SHEETS
GASEOUS ORGANIC ANALYSIS-GC METHOD

C. Sampling Considerations

Location to Set Up GC ______________________________

____

Special Hazards to be Considered ______________________________

____

Power Available at Duct ______________________________

Power Available for GC ______________________________

Plant Safety Requirements ______________________________

____

Vehicle Traffic Rules ______________________________

____

Plant Entry Requirements ______________________________

____

Security Agreements ______________________________

____

Potential Problems ______________________________

____

D. Site Diagrams. (Attach Additional Sheets if Required).

Figure 3(Continued). Preliminary survey data sheet.

Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to maintain a slight positive nitrogen pressure. Secure the stopcocks with tape and take into the field.

The grab samples can be obtained either (1) by drawing the gases into an evacuated flask or (2) by drawing the gases into and purging the flask with a rubber suction bulb. The procedures are discussed below.

2.2.1.1 Evacuated Flask Procedure

With a high-vacuum pump, evacuate the flask to the capacity of the pump; then close off the stopcock leading to the pump. Attach a 6-mm-OD glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6-mm-OD Pyrex sampling probe, enlarged at one end to a 12-mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent movement during shipment. Measure and record the duct temperature and pressure.

2.2.1.2 Gas Collecting Tube Procedure

Attach one end of the gas collecting tube to a rubber suction bulb. Attach the other end to a 6-mm-OD glass probe as described in Section 2.2.1.1. Place the particulate filter end of the probe at the centroid of the duct and apply suction with the bulb to completely purge the probe and gas collecting tube. After the gas collecting tube has been purged, close off the stopcock near the suction bulb and then close the stopcock near the probe. Remove the probe from the duct and disconnect both the probe and suction bulb. Tape the stopcocks to prevent movement during shipment. Measure and record the duct temperature and pressure.

2.2.2 Collection of Grab Samples - Flexible Bags

Tedlar or aluminized Mylar bags can also be used to obtain the presurvey grab sample. Use new bags and leak check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air, and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Details of the leak check and the bag collection procedures are given in Section 2.4.2.

2.2.3 Determination of Moisture Content

For combustion or water-controlled processes, obtain the moisture content from plant personnel or by measurement during the presurvey. If the source is below 50°C, measure the wet bulb and dry bulb temperatures and calculate the moisture content using a psychrometric chart. At higher temperatures, determine the moisture content using EPA Method 4.

2.2.4 Determination of Static Pressure

Obtain the static pressure from the plant personnel or measure it. If a type S pitot tube and an inclined manometer are used, position the pitot tube 90 degrees from the flow in the source. Disconnect one of the tubes connecting the pitot tube to the manometer and read the static pressure. Note which leg of the pitot is disconnected in order to determine the correct sign (positive or negative).

2.2.5 Grab Sample Analysis

Before analysis, heat the grab sample to the duct temperature to vaporize any condensed material. Analyze the samples by the GC/FID procedure and compare the retention times against the artificial samples containing the components expected to be in the stream. If any compounds cannot be identified with certainty by this procedure, identify them by other means such as GC/MS or GC/infrared technique. If a GC/MS system is available, this method is recommended.

2.3 PRELIMINARY METHOD DEVELOPMENT EVALUATION

Once the stack temperature, static pressure, moisture content, approximate particulate concentration, and the identify and approximate concentration of the components are known, one can determine the sampling system, GC column, and approximate analytical conditions (flow rate and ignition port, column, and detector temperatures).

2.3.1 Choice of GC Conditions

Using the expected source gas composition from the pretest survey and basic chromatography knowledge (see Appendix A), select possible GC columns that will provide the necessary peak resolution and shape consistent with good GC techniques. Record the chosen GC conditions on a data sheet such as shown in Figure 4.

Since emissions from organic sources vary widely in composition, details of an analytical scheme that is suitable for every source cannot be provided here. Generally, if the GC is used in an isothermal mode, the column temperature should provide good peak resolution and a reasonable time for the total analysis. Column flow rates of 20 to 40 ml/min are typical at head pressures of 20 to 40 psig. Analysis of aliphatic hydrocarbons (C_1 to C_4) using a 1.8-m by 3.13-mm hromosorb 102 column can be carried out at column temperature between 80° and 120°C. Aromatic hydrocarbons, including benzene, toluene, and xylenes, can be successfully chromatographed at 80°C using a 1.8-m by 3.13-mm 10 percent DC-200 on Chromosorb WHP column. Some other recommended columns include: 1.8-m by 3.13-mm Chromosorb 102 for low molecular weight hydrocarcons, 1.8-m by 3.13-mm 10 percent DC-200 silicone oil on 80 to 100 mesh Chromosorb WHP for aromatic and chlorinated compounds, and 1.8-m by 3.13-mm Tenax GC or 1.8-m by 3.13-mm Dexsil 400 for a variety of nonpolar and polar compounds.

Verify the choice of column, temperature, and other instrument parameters in the laboratory before any field sampling as follows:

Gaseous Organic Analysis - Chromatographic Conditions

Gas Chromatographic Conditions

Components to be Analyzed	Expected Concentration

Suggested Chromatographic Column ____________________

____

Column flow rate ____ml/min Head pressure____psig

Column temperature:

Isothermal __________°C

Programmed from _____°C to ____°C at ____°C/min

Injection port/sample loop temperature ______°C

Detector temperature _______°C

Detector flow rates: Hydrogen _____ml/min.

head pressure____psig

Air/Oxygen _____ml/min,

head pressure____psig

Chart speed __________ inches/minute

Compound data:

Compound	Retention Time	Attenuation

Figure 4. Chromatographic conditions for gaseous organic analysis.

Compare the chromatograms from the pretest grab sample and a synthetic mixture of the expected components. Use this mixture also to refine the instrument conditions and establish a calibration curve. If dilution is required, determine the dilution factor and assemble the sampling apparatus to provide the required dilution.

2.3.2 Calibration Gases

If available, use NBS reference gases or commercial gas mixtures certified through direct analysis for the calibration curves. Aliphatic hydrocarbons in an inert gas matrix are available. If commercial mixtures are not available, then prepare and verify standards both internally in the laboratory and through an external source in order to provide a quality control check.

2.3.2.1 Preparation of Standards From Volatile Materials

The following technique for preparing standards, which is an adaptation of EPA Method 106 for vinyl chloride, is recommended:

2.3.2.1.1 Bag Technique

Evacuate a 16-inch square Tedlar bag that has passed a leak check (see Section 2.4.2), and meter in 5.0 liters of nitrogen through a 0.5-liter/revolution dry test meter. While the bag is filling, use a 0.5-ml syringe to inject a known quantity of the material of interest through the wall of the bag or through a septum-capped tee at the bag inlet. Upon withdrawing the syringe needle, immediately cover the resulting hole with a piece of masking tape. In a like manner, prepare dilutions having other concentrations. Prepare a minimum of three concentrations.

Place each bag on smooth surface and alternately depress opposite sides of the bag 50 times to mix the gases. Record the average meter temperature, gas volume, liquid volume, barometric pressure, and meter pressure.

Set the electrometer attenuator to the X1 position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the injection time, sample loop temperature, column temperature, carrier gas flow rate, chart speed, and attenuator setting. Record peaks and detector responses that occur in the absence of any sample. Maintain conditions. Flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the calibration mixtures, and open the sample valve. Record the injection time. Select the peak that corresponds to the compound of interest. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This quantity, divided by the chart speed, is defined and recorded as the retention time.

To prepare the GC calibration curve, make a GC measurement of each of the standard gas mixtures described above. Record the concentrations injected, the attenuator setting, chart speed, peak area, sample-loop temperature, column temperature, carrier-gas flow rate, and retention time. Record the laboratory pressure. Calibrate the peak area multiplied by the attenuator setting. Repeat until the area of two consecutive sample injects agree within 5 percent, then plot the average versus the concentration.

When the other concentrations have been plotted, draw a line through the points derived by the least squares method. Perform the calibration daily, or before and after each set of bag samples, whichever is more frequent. Record all data as shown on the example data sheet in Figure 5.

2.3.2.1.2 Cylinder Approach

As an alternative procedure, maintain high and low calibration standards. Use the high-concentration (50 to 100 ppm) standard to prepare a three-point calibration curve using an appropriate dilution technique. Then use the low-concentration standard to verify the dilution technique. Use this same approach also to verify the dilution techniques for high-concentration source gases.

To prepare the diluted calibration samples, use calibrated rotameters to meter both the high-concentration calibration gas and the diluent gas. Adjust the flow rates through the rotameters with micrometer valves to obtain the desired dilutions. A positive displacement pump or other metering technique may be used in place of the rotameter to provide a fixed flow of high-concentration gas.

To calibrate the rotameters, connect each rotameter between the diluent gas supply and a suitably sized bubble meter, spirometer, or wet test meter. While it is desirable to calibrate the calibration gas flow meter with the calibration gas, generally the available amount of this gas will preclude it. The error introduced by using the diluent gas is insignificant for gas mixtures of up to 1000 to 2000 ppm of each component. Record the temperature and atmospheric

Calibration Curve Data - Volatile and Liquid Samples Collected in a Tedlar Bag

	Blank	Mixture 1	Mixture 2	Mixture 3
Size of Tedlar bag (inches)	___	___	___	___
Dilution gas (name)	___	___	___	___
Vol. of dilution gas (liters)		___	___	___
Component (name)		___	___	___
Volume of component (ml)		___	___	___
Average meter temp. (°C)		___	___	___
Average meter pressure (mm)		___	___	___
Atmospheric pressure (mm)		___	___	___
Density of liquid component (g/ml)		___	___	___
Sample loop volume (ml)	___	___	___	___
Sample loop temp. (°C)	___	___	___	___
Carrier gas flow rate (ml/min)	___	___	___	___
Column temperature				
initial (°C)	___	___	___	___
program rate (°C/min)	___	___	___	___
final (°C)	___	___	___	___
Injection time (24 hr. basis)	___	___	___	___
Distance to peak (inches)	___	___	___	___
Chart speed (inch/min)	___	___	___	___
Retention time (min)	___	___	___	___
Concentration of component (ppm)	___	___	___	___
Attenuator setting	___	___	___	___
Peak height (mm)	___	___	___	___
Peak area (mm²)	___	___	___	___
Area x attenuation	___	___	___	___

Plot peak area x attenuation against concentration to obtain calibration curve.

Figure 5. Calibration curve data sheet - injection of volatile sample into Tedlar bag.

Audit Samples	Sample 1	Sample 2
Retention time (min)	________	________
Injection time (24-hr basis)	________	________
Attenuation factor	________	________
Peak height (mm)	________	________
Peak area (mm^2)	________	________
Peak area x attenuation factor	________	________
Measured concentration (ppm)	________	________
Data reported on (date)	________	________
Data reported by (initial)	________	________
Certified Concentration (ppm)	________	________
Deviation (%)	________	________

Figure 5 (continued). Calibration curve data sheet - injection of volatile sample into Tedlar bag.

pressures during calibration. Calibrate the rotameter over the entire flow range with a minimum of 5 flow rates. Plot the rotameter readings against the actual flow rate and record the temperature and atmospheric pressure on each calibration curve. Record all data on a data sheet as shown in Figure 6.

Correct the flow rate to different temperatures and atmospheric pressures as follows:

$$Q_{T_2P_2} = Q_{T_1P_1}\left(\frac{P_2T_1}{P_1T_2}\right)^{1/2}$$

Where:

$Q_{T_2P_2}$ = Flow rate at new absolute temperature (T_2) and new absolute pressure (P_2).

$Q_{T_1P_1}$ = Flow rate at calibration absolute temperature (T_1) and absolute pressure (P_1).

Connect the rotameters to the calibration and diluent gas supplies using 6-mm Teflon tubing. Connect the outlet side of the rotameters through a connector to a leak-free Tedlar bag as shown in Figure 7. (See Section 2.4.2 for leak check procedure.) Adjust the gas flows to provide the desired dilution and fill the bag with sufficient gas for calibration, being careful not to fill to the point where it applies additional pressure on the gas. Record the flow rates

Rotameter Calibration Data

Rotameter number ______________________________

Gas used ______________________________

Method: Bubble meter ______ Spirometer ______ Wet test meter ______

Rotameter construction ______________________________

Float type ______________________________

Laboratory temperature (T obs.) ________ °C ________ °F

Laboratory pressure (P obs.) _____ in Hg ________ mm Hg

1.

Flow Meter Reading	Time (min)	Gas Volume[a]	Flow Rate (Lab Conditions)[b]

[a] Vol. of gas may be measured in milliliters, liters or cubic feet

[b] Convert to Standard Conditions (20°C and 760 mm Hg)

$$Q_{STD} = Q_{obs} \left(\frac{760 \times T\ obs.}{P\ obs. \times 20}\right)^{1/2}$$

Flow Meter Reading	Flow Rate (STD Conditions)

Plot meter reading against flow rate (std) and draw smooth curve.

Figure 6. Rotameter calibration data sheet.

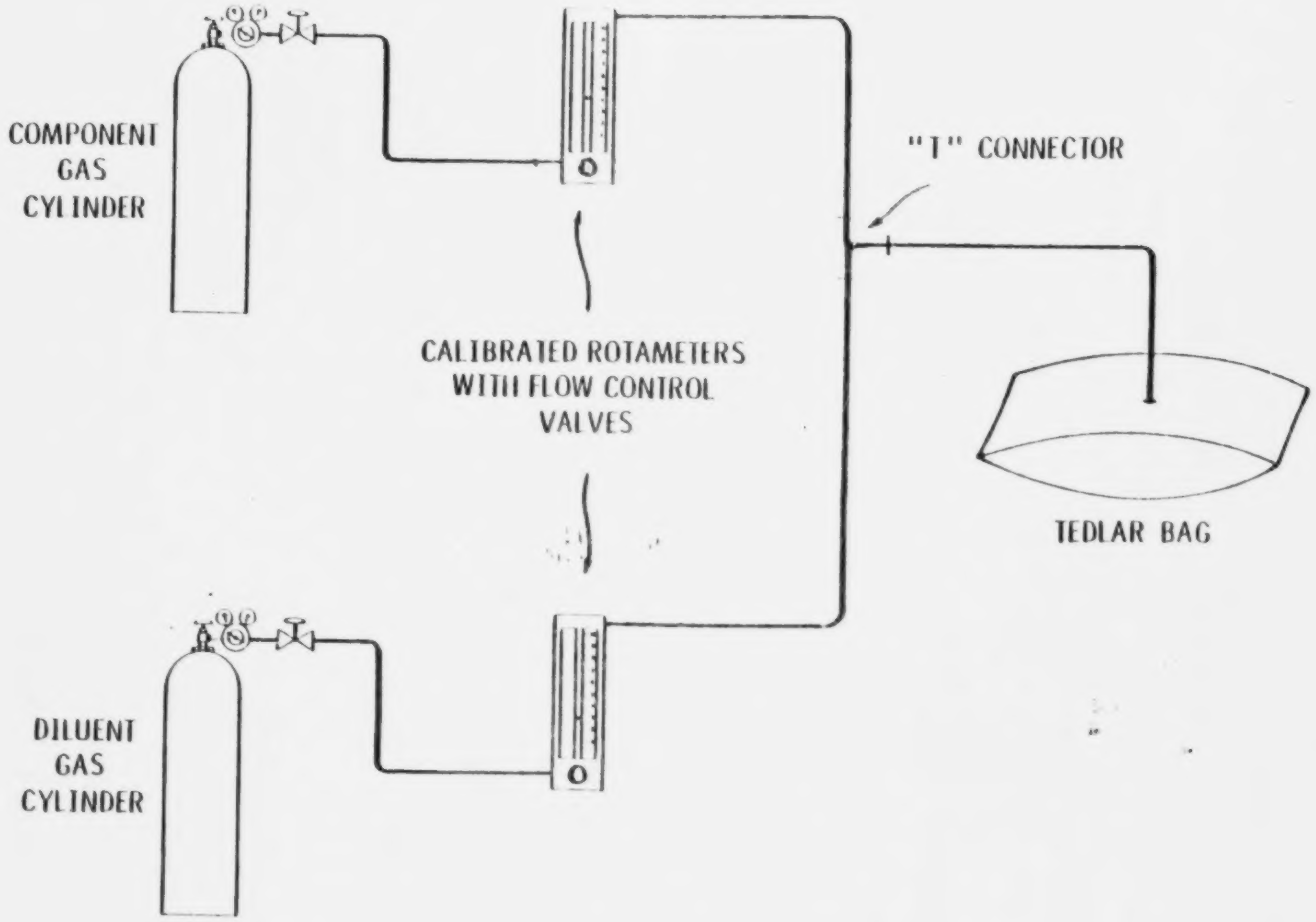

COMPONENT
GAS
CYLINDER
CALIBRATED ROTAMETERS
WITH FLOW CONTROL
VALVES
"T" CONNECTOR
TEDLAR BAG
DILUENT
GAS
CYLINDER

Figure 7. Single-stage calibration gas dilution system.

of both rotameters, the ambient temperature, and atmospheric pressure. Calculate the concentration of diluted gas as follows:

$$C_a = \frac{10^6 \times \overline{X} q_a}{q_D}$$

Where:

C_a = Concentration of component a in ppm.

q_a = Flow rate of component a at measured temperature and pressure.

q_D = Diluent gas flow at measured temperature and pressure.

$\overline{X}$ = Mole fraction of component in the calibration gas to be diluted.

Use single-stage dilutions to prepare calibration mixtures up to about 1:20 dilution factor. For greater dilutions, use a double dilution system. Assemble the apparatus as shown in Figure 8, using calibrated flow meters of suitable range. Adjust the control valves so that about 90 percent of the diluted gas from the first stage is exhausted and 10 percent goes to the second stage flow meter. Fill the Tedlar bag with the dilute gas from the second stage. Record the temperature, ambient pressure, and water manometer pressure readings. Correct the flow reading in the first stage as

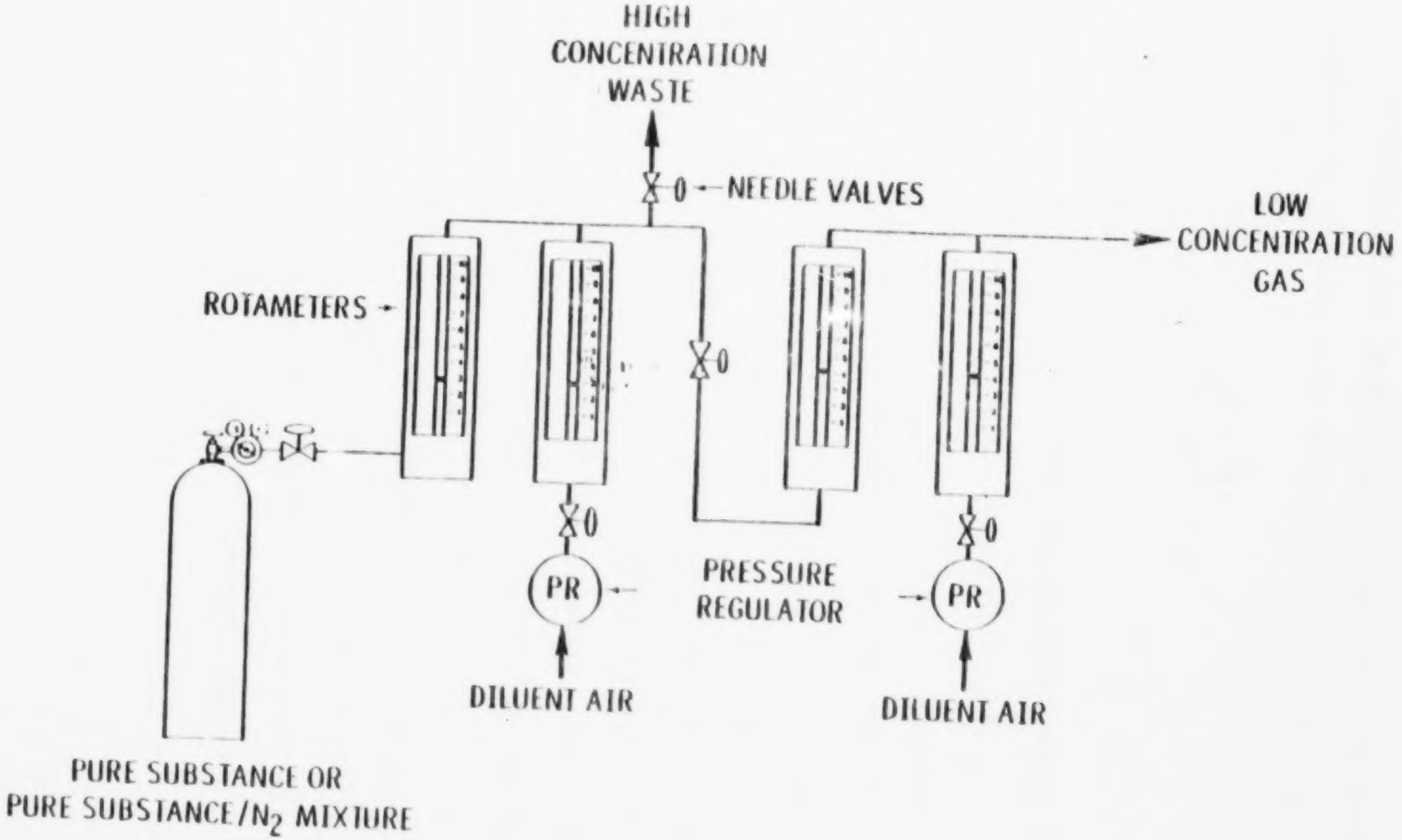

HIGH
CONCENTRATION
WASTE
NEEDLE VALVES
LOW
CONCENTRATION
GAS
ROTAMETERS
PR
PR
PRESSURE
REGULATOR
DILUENT AIR
DILUENT AIR
PURE SUBSTANCE OR
PURE SUBSTANCE/N_2 MIXTURE

Figure 8. Two-stage dilution apparatus.

indicated by the water manometer reading. Calculate the concentration of the component in the final gas mixture as follows:

$$C_a = 10^6 \, \overline{X} \left[\frac{qa_1}{qa_1 + qD_1} \right] \left[\frac{qa_2}{qa_2 + qD_2} \right]$$

Where:

C_a = Concentration of component "a" in ppm.

$\overline{X}$ = Mole fraction of component "a" in original gas.

qa_1 = Flow rate of component "a" in stage 1.

qa_2 = Flow rate of component "a" in stage 2.

qD_1 = Flow rate of diluent gas in stage 1.

qD_2 = Flow rate of diluent gas in stage 2.

Prepare three calibration gas mixtures, one at the approximate concentration expected to be found in the source, and one higher and one lower than this concentration. Analyze the calibration gas mixtures using the specified column and conditions with the FID. Plot the peak heights (or peak area) against the concentration and draw a straight line through the points derived by the least squares method. Analyze the low-concentration standard using the same instrument conditions, and read the value from the curve. The analyzed value and the known concentration should agree to within 5 percent. If this agreement is not obtained, run additional dilutions to obtain this agreement. Record all data on a data sheet as shown in Figure 9.

Calibration Curve Data - Dilution Method

1. High Concentration Gas Mixture

Component ________________ Concentration ____________ppm

Diluent gas ______________

2. Dilution and Analysis Data

Date ______________

Stage 1	Mixture 1	Mixture 2	Mixture 3
Component gas-rotameter reading			
Diluent gas-rotameter reading			
Ambient temp. (°C)			
Manometer reading, inches H_2O			
Flow rate component gas (ml/min)			
Flow rate diluent gas (ml/min)			

Stage 2	Mixture 1	Mixture 2	Mixture 3
Component gas-rotameter reading			
Diluent gas-rotameter reading			
Flow rate component gas (ml/min)			
Flow rate diluent gas (ml/min)			
Calculated concentration (ppm)			

Analysis	Mixture 1	Mixture 2	Mixture 3
Sample loop volume (ml)			
Sample loop temp. (°C)			
Carrier gas flow rate (ml/min)			
Column temperature			
initial (°C)			
program rate (°C/min)			
final (°C)			
Injection time (24-hr basis)			
Distance to peak (inches)			
Chart speed (inch/min)			
Retention time (min)			
Attenuator factor			
Peak height (mm)			
Peak area (mm^2)			
Area x attenuation factor (mm^2)			

Plot peak area x attenuator factor against concentration to obtain calibration curve.

Figure 9. Calibration curve data sheet - dilution method.

3. Low Concentration Standard

Known concentration (ppm) __________
Retention time (min) __________
Injection time (24-hr basis) __________
Attenuation factor __________
Peak height (mm) __________
Peak area (mm^2) __________
Peak area x attenuation (mm^2) __________
Calculated concentration (ppm) __________
Deviation (%) __________

4. Audit Samples

	Sample 1	Sample 2
Retention time (min)		
Injection time (24-hr basis)		
Attenuation factor		
Peak height (mm)		
Peak area (mm^2)		
Peak area x attenuation factor		
Measured concentration		
Data reported on (date)		
Data reported by (initial)		
Certified concentration (ppm)		
Deviation (%)		

Note: If a pump is used instead of a rotameter for component gas flow, substitute pump delivery rate for rotameter readings).

Figure 9 (continued). Calibration curve data sheet - dilution method.

Further details of the calibration methods for rotameters and the dilution system can be found in Nelson's "Controlled Test Atmospheres, Principles and Techniques."

As previously mentioned, a positive displacement pump can be used to control the flow rate of the high-concentration calibration gas, with a rotameter to measure the flow of the diluent gas. This procedure can be used for both one- and two-stage dilutions following the method outlined above.

Check the relative peak area of the calibration standards daily to guard against degradation. If the relative peak areas on successive days differ by more than 5 percent, remake the standards before proceeding to the field analysis.

2.3.2.2 Preparation of Standards From Less Volatile Liquid Materials

Use the equipment shown in Figure 10. Calibrate the dry gas meter with a wet test meter or a spirometer. Use a water manometer for the pressure gauge and glass, Teflon, brass, or stainless steel for all connections. Connect a valve to the inlet of the 50-liter Tedlar bag.

To prepare the standards, assemble the equipment as shown in Figure 10 without the bag and leak check the system. Completely evacuate the bag. Fill the bag with hydrocarbon-free air, and evacuate the bag again. Close the inlet valve.

Turn on the hot plate and allow the water to reach boiling. Connect the bag to the impinger outlet. Record the initial meter reading, open the bag inlet valve, and open the cylinder. Adjust

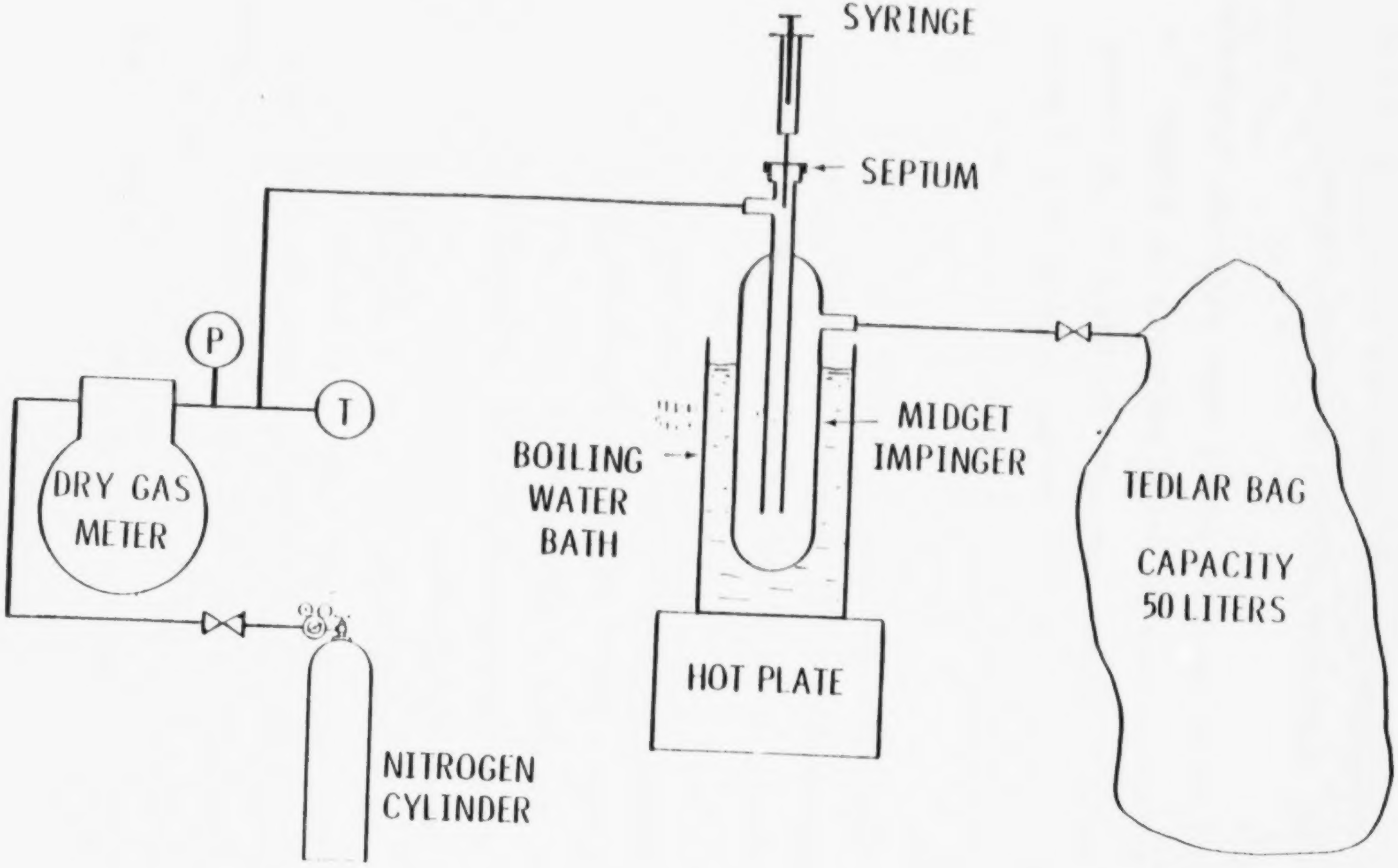

SYRINGE
SEPTUM
P
T
DRY GAS METER
BOILING WATER BATH
MIDGET IMPINGER
TEDLAR BAG
CAPACITY 50 LITERS
HOT PLATE
NITROGEN CYLINDER

Figure 10. Apparatus for preparation of liquid materials.

the rate so that the bag would be completely filled in approximately 15 minutes. Record meter pressure, temperature, and local barometric pressure.

Fill the syringe to the desired liquid volume with the material to be evaluated. Place the syringe needle into the impinger inlet using the septum provided, and inject the liquid into the flowing air stream. Use a needle of sufficient length to permit injection of the liquid below the air inlet branch of the tee. Remove the syringe.

Complete filling of the bag; note and record the meter pressure and temperature at regular intervals, preferably 1 minute.

When the bag is filled, stop the pump and close the bag inlet valve. Record the final meter reading.

Disconnect the bag from the impinger outlet, and set it aside for at least 1 hour to equilibrate. Analyze the sample within the proven life period of its preparation.

Average the meter temperature (T_m) and pressure (P_m) readings over the bag filling process.

Measure the solvent liquid density at room temperature by accurately weighing a known volume of the material on an analytical balance to the nearest 1.0 milligram. Take care during the weighing to minimize evaporation of the material. A ground-glass stoppered 25-ml volumetric flask or a glass-stoppered specific gravity bottle is suitable for weighing. Calculate the result in terms of g/ml.

As an alternative, literature values of the density of the liquid at 20°C may be used.

Calculate the concentration of material in the sample in mg/liter at standard conditions as follows:

$$C_{std\ sol} = \frac{2593\ (L_v)\ (p)\ (293 + T_m)}{(M_f - M_i)\ (P_{bar} + P_m)}$$

Where:

$C_{std\ sol}$ = Standard solvent concentration, mg/std liter.

p = Liquid density at room temperature, g/ml.

L_v = Liquid volume inected, ml.

T_m = Meter temperature, °C.

P_m = Meter pressure (gauge), mm Hg.

P_{bar} = Local barometric pressure (absolute), mm Hg.

M_f, M_i = Final and initial meter reading, liters.

Continue the procedure as described in preparing the volatile standard (Section 2.3.2.1), and record all data on the sheets shown in Figure 5.

2.3.3 Evaluation of Calibration and Analysis Procedure

Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Supplement B: "Procedure for Field Auditing GC Analysis." The information required to document the analysis of the audit samples has been included on the example data sheets shown in Figures 5 and 9 and Supplement I-B. The audit analyses must agree with the audit concentrations within ± 10 percent. Testers may obtain audit cylinders by contacting: Environmental Protection Agency, Environmental Monitoring Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at the Environmental Protection Agency, the tester must secure them from an alternative source.

2.4 SAMPLING AND ANALYSIS PROCEDURE

Considering safety (flame hazards) and the source conditions, select an appropriate sampling method. In situations where a hydrogen flame is a hazard and no intrinsically safe GC is available, use the bag collection technique or one of the adsorption techniques. If no prohibitions against the hydrogen flame exist, the source temperature is below 100°C, and the organic concentrations are low enough to prevent detector saturation, use the direct interface method. If the source gases require dilution, use either the bag sample or adsorption tubes with the dilution interface. The choice between these two techniques will depend on the physical layout of the site, the source temperature, and the storage stability of the compounds if collected in the bag. Sample polar compounds by direct interfacing or dilution interfacing to prevent loss by adsorption on the bag.

2.4.1 Adsorption Tube Method

Refer to the National Institute for Occupational Safety and Health (NIOSH) method for the particular organics to be sampled.

The principal interferent will be water vapor. If water vapor is present at concentrations above 3 percent, silica gel must be used in front of the charcoal. Where more than one compound is present in the emissions, then relative adsorptive capacity information must be developed.

Refer to the NIOSH method to determine the equipment required for the particular organic(s) to be sampled. The following items are also required.

Probe. Borosilicate glass, stainless steel, or Teflon, approximately 6-mm ID, with a heating system if water condensation could be a problem, and a filter (either in-stack or heated out-stack) to remove particulate matter if it is present. A plug of glass wool is a satisfactory filter.

Sample Pump. Positive displacement type, with flow totalizer, pumping rate approximately 10-100 cc/min with a set of limiting orifices, MDA Scientific Model 808, or equivalent.

Adsorption Tubes. Similar to ones specified by NIOSH, except adsorbent per section 200/800 mg for charcoal tubes and 260/1040 mg for silica gel tubes.

Barometer. Accurate to 5 mm Hg, to measure a atmospheric pressure during sampling and pump calibration.

Follow the sampling and analysis portions of the NIOSH method section entitled "Procedure." Use a sample probe, if required. The gas to be sampled must be provided at atmospheric pressure, or slightly above it. Record the total volume of gas sampled, or the number of pump strokes, and the barometric pressure. Obtain a total sample volume commensurate with the expected concentration(s) of the volatile organic(s) present. Laboratory tests prior to actual sampling may be necessary to accurately predetermine this number.

Operate the gas chromatograph according to the manufacturer's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Repeat the analysis until two consecutive injections do not deviate in area more than 2 percent from their average.

Standards shall be prepared according to the respective NIOSH method. A minimum of three different standards shall be used, and they shall bracket the expected sample concentration. Calibration is to be performed before and after each day's sample analysis work. Prepare a calibration curve derived by the least square method.

Either before or after actual sampling, determine the desorption efficiency of each batch of adsorption media according to the respective NIOSH method. Use an internal standard.

Immediately before the sample analyses, perform analyses on the two audits in accordance with Supplement I-B. The audit analysis must agree with the audit concentration within ± 10 percent.

2.4.2 Integrated Bag Sampling and Analysis

2.4.2.1 Evacuated Container Method

In this method, the bags are filled by evacuating the rigid air-tight container holding the bags. As a result, both the bags and the container must be checked for leaks before and after use, as follows: Connect a water manometer using a tee connector between the bag or rigid container and a pressure source. Pressurize the bag or container to 5 to 10 cm H_2O (2 to 4 in. H_2O), and allow it to stand overnight. A deflated bag indicates a leak.

The following equipment is required for the evacuated container method:

Probe - stainless steel, Pyrex glass, or Teflon tubing according to the duct temperature, 6.4-mm-OD tubing of sufficient length to connect to the sample bag. Use stainless or Teflon unions to connect probe and sample line.

Quick connects - male (2) and female (2) of stainless steel construction.

Needle valve - to control gas flow.

Pump - leakless Teflon-coated diaphragm-type pump or equivalent to deliver at least 1 liter/min.

Charcoal adsorption tube - tube filled with activated charcoal and glass wool plugs at each end to adsorb organic vapors.

Flow meter - 0 to 500-ml flow range; manufacturer's calibration curve is adequate.

To obtain a sample, assemble the sample train as shown in Figure 11. Leak check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack and start the pump

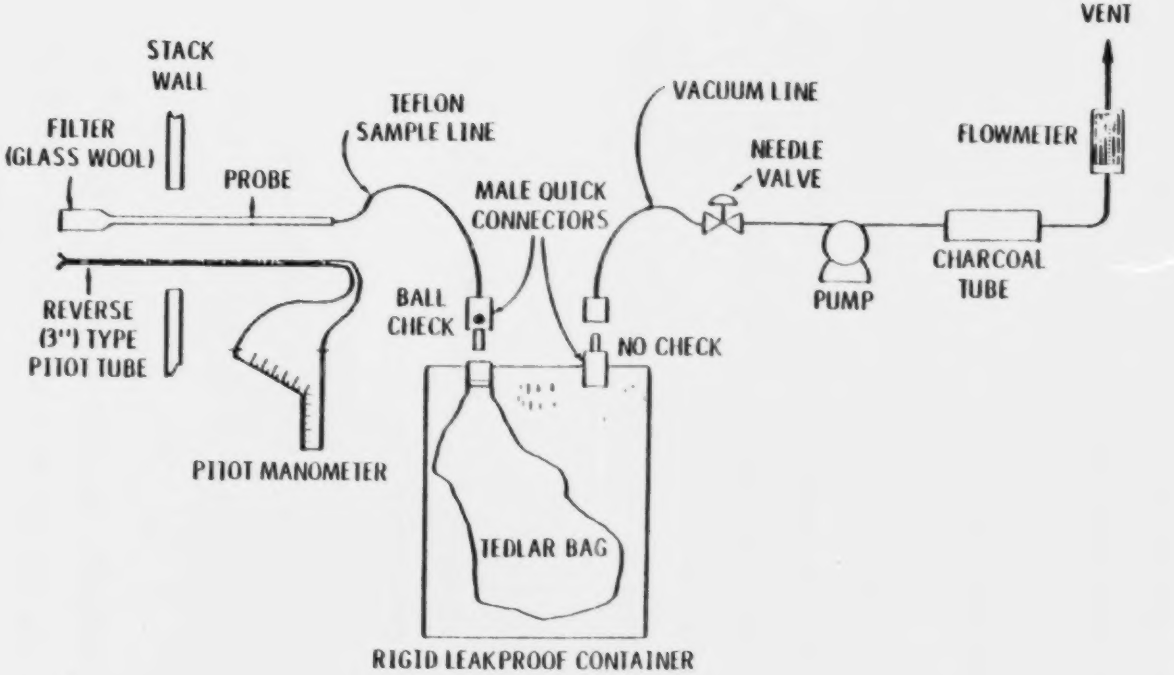

STACK WALL
FILTER (GLASS WOOL)
PROBE
TEFLON SAMPLE LINE
REVERSE (3") TYPE PITOT TUBE
PITOT MANOMETER
BALL CHECK
MALE QUICK CONNECTORS
NO CHECK
TEDLAR BAG
RIGID LEAKPROOF CONTAINER
VACUUM LINE
NEEDLE VALVE
PUMP
CHARCOAL TUBE
FLOWMETER
VENT

Figure 11. Integrated bag sampling train.

with the needle valve adjusted to yield a flow of 0.5 liter/minute. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag and evacuate until the rotameter indicates no flow. Then reposition the sample and vacuum lines, and begin the actual sampling, keeping the rate proportional to the stack velocity. Direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, batometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in Figure 12. Protect the Tedlar bag and its container from sunlight. When possible, perform the analysis within 8 hours of sample collection.

2.4.2.2 Direct Pump Method

Follow 2.4.2.1, except place the pump and needle valve between the probe and the bag. The pump and needle valve must be constructed of stainless steel or some other material that is not affected by the stack gas. The system must be adequately leak checked and then purged with stack gas before the connection to the previously evacuated bag is made.

2.4.2.3 Analysis of Bag Samples

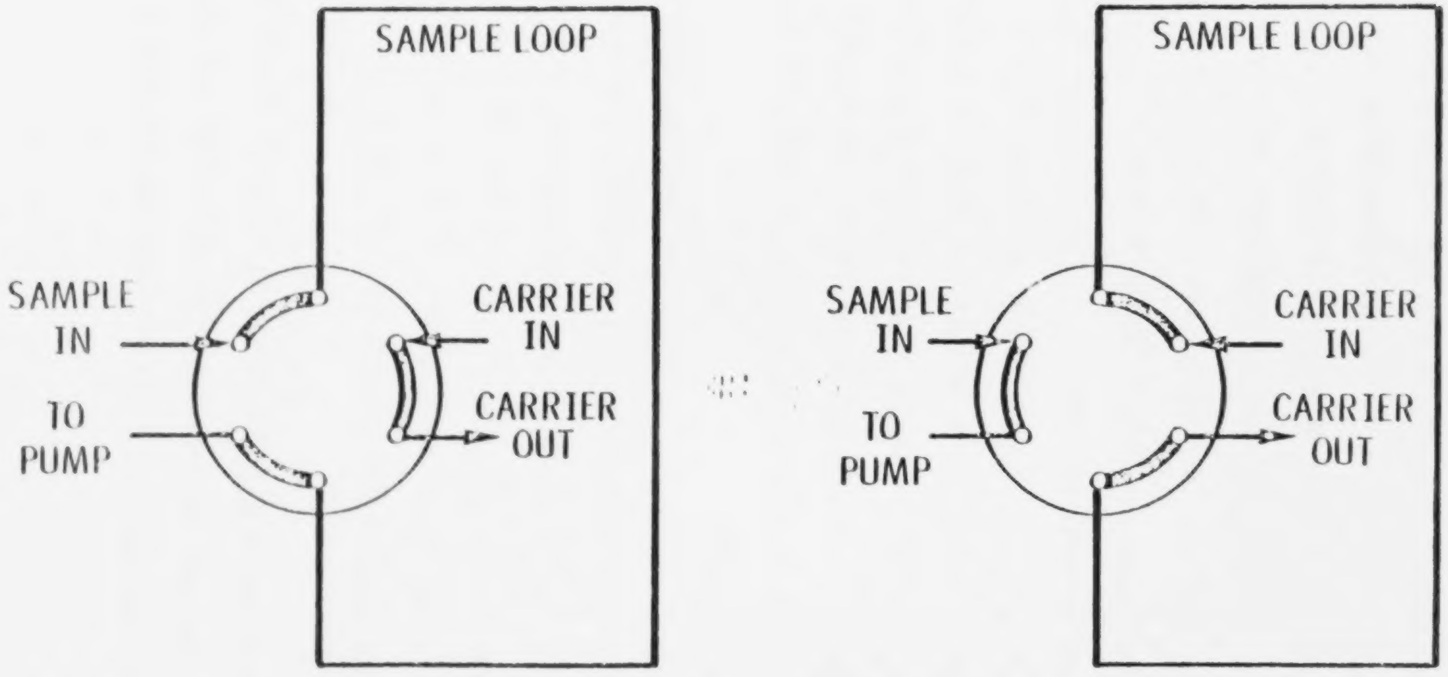
Connect the needle valve, pump, charcoal tube, and flow meter to draw gas samples through the gas sampling valve. The operation of the gas sampling valve is shown in Figure 13. Flush the sample loop with gas from one of the three Tedlar bags containing

Plant______________________________ Date______________

Site____

	Sample 1	Sample 2	Sample 3
Source temperature (°C)	________	________	________
Barometric pressure (mm)	________	________	________
Ambient temperature (°C)	________	________	________
Sample flow rate	________	________	________
Bag number	________	________	________
Start time	________	________	________
Finish time	________	________	________

Figure 12. Field sample data sheet - Tedlar bag collection method.


SAMPLE LOOP
SAMPLE IN
TO PUMP
CARRIER IN
CARRIER OUT
SAMPLE LOOP
SAMPLE IN
TO PUMP
CARRIER IN
CARRIER OUT

PURGE POSITION

SAMPLE INJECTION POSITION

Figure 13. Gas sampling valve operation.

calibration mixture, and analyze the sample. Obtain at least two chromatograms for the sample. The results are acceptable if the peak areas agree to within 5 percent. If they do not agree, run additional samples until consistent area data are obtained. If this agreement is not obtained, correct the instrument technique problems before proceeding. If the results are acceptable, analyze the other two calibration gas mixtures in the same manner. Calculate and draw the calibration line.

Analyze the two field audit samples (see Supplement I-B) by connecting each Tedlar bag containing an audit gas mixture to the sampling valve, following the guidelines used for the calibration gases. Calculate the results; record and report the data to the audit supervisor. If the results are acceptable, proceed with the analysis of the source samples.

Analyze the source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified with that bag. Follow the restrictions on replicate samples specified for the calibration gases. Record the data. Analyze the other two bag samples of source gas in the same manner. After all three bag samples have been analyzed, repeat the analysis of the calibration gas mixtures.

An example field analytical data sheet is shown in Figure 14. The sheet has been designed to tabulate information from the bag collection, direct interface, and dilution interface systems; as a

Gaseous Organic Sampling and Analysis Data

Plant ______________________________ Date ______________

Location ____

1. General Information

Source temperature (°C) __________

Probe temperature (°C) __________

Ambient temperature (°C) __________

Atmospheric pressure (mm) __________

Source pressure ("Hg) __________

Absolute source pressure (mm) __________

Sampling rate (liter/min) __________

Sample loop volume (ml) __________

Sample loop temperature (°C) __________

Columnar temperature:

    Initial (°C)/Time (min) __________

    Program Rate (°C/min) __________

    Final (°C)/Time (min) __________

Carrier gas flow rate (ml/min) __________

Detector temperature (°C) __________

Injection time (24 hr. basis) __________

Chart speed (mm/min) __________

Dilution gas flow rate (ml/min) __________

Dilution Gas used (symbol) __________

Dilution ratio __________

Figure 14. Field analysis data sheets.

2. Field Analysis Data - Calibration Gas

Run No.__________ Time__________

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No.__________ Time__________

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No.__________ Time__________

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Figure 14 (continued). Field analysis data sheets.

3. Field Analysis Data - Audit Samples Cylinder No. __________

Run No. __________ Time __________

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No. __________ Time __________

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No. __________ Time __________

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Figure 14 (continued). Field analysis data sheets.

4. Field Analysis Data - Source Gas

Run No.__________ Time__________

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No.__________ Time__________

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Run No.__________ Time__________

Components	Area	Attenuation	A x A Factor	Conc. (ppm)

Figure 14 (continued). Field analysis data sheets.

result, not all of the requested information will apply to any single method. Note the data that do not apply with the notation "N.A."

2.4.3 Direct Interface Sampling and Analysis

Use the direct interface sampling method whenever possible, provided that the moisture content of the gas will not interfere with the analytical method, the physical requirements of the equipment can be met at the site, and the source gas concentration is low enough that detector saturation is not a problem. The equipment required for this method is as follows:

Probe - stainless steel, Pyrex glass, or Teflon tubing as required by duct temperature, 6.4-mm OD enlarged at duct end to contain glass wool plug. Probe should be heated with heating tape or a special heating unit capable of maintaining duct temperature. The heating unit can be controlled with a variable transformer or with a temperature controller/readout device.

Sample lines - 6.4-mm-OD Teflon lines, heat-traced to prevent condensation of material.

Quick connects - to connect sample line to gas sampling valve on GC instrument and to pump unit used to withdraw source gas. A quick connect should also be provided on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

Thermocouple readout device - potentiometer or digital thermometer to measure source temperature and probe temperature.

Heated gas sampling valve - of two-position, six-port design, as shown in Figure 13, to allow sample loop to be purged with source gas or to direct source gas into the GC.

Needle valve - to control gas sampling rate from the source.

Pump - leakless Teflon-coated diaphragm-type pump or equivalent, capable of at least 1 liter/minute sampling rate.

Flow meter - of suitable range to measure sampling rate.

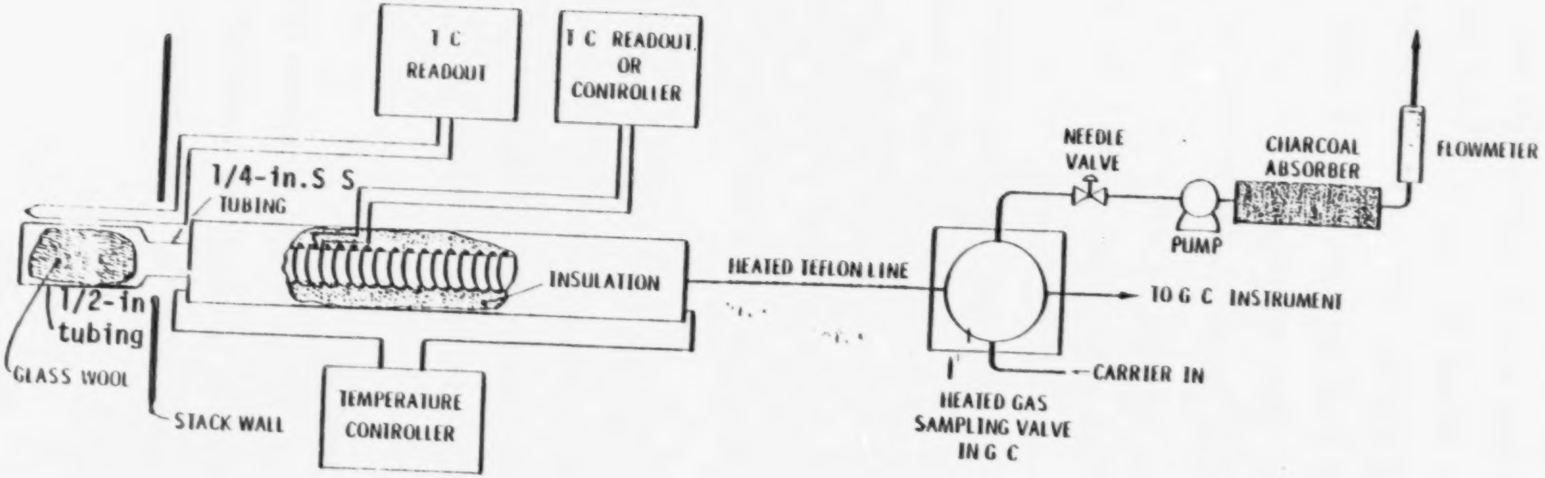
Charcoal adsorber - to adsorb organic vapor collected from the source to prevent exposure of personnel to source gas.

Gas cylinders - of carrier gas (helium or nitrogen), oxygen, and hydrogen for the FID.

Gas chromatograph - instrument capable of being moved into the field with a FID, heated gas sampling valve, column required to complete separation of desired components, and option for temperature programming. Other dectors can be used for problem analyses.

Recorder/Integrator - to record and/or calculate results.

To obtain a sample, assemble the sampling system as shown in Figure 15. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the source temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature of 0-3°C above the source temperature. While the probe and heated line are being heated, disconnect the sample line from



T C
READOUT
T C READOUT
OR
CONTROLLER
1/4-in.S S
TUBING
INSULATION
1/2-in
tubing
GLASS WOOL
STACK WALL
TEMPERATURE
CONTROLLER
HEATED TEFLON LINE
NEEDLE
VALVE
PUMP
CHARCOAL
ABSORBER
FLOWMETER
TO G C INSTRUMENT
CARRIER IN
HEATED GAS
SAMPLING VALVE
IN G C

Figure 15. Direct interface sampling system.

the gas sampling valve and attach the line from the calibration gas mixture. Flush the sample loop with calibration gas and analyze a portion of that gas. Record the results. After the calibration gas sample has been flushed into the GC instrument, turn the gas sampling valve to flush position, then reconnect the probe sample line to the valve. Move the probe to the sampling position and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the sample using the same conditions as for the calibration gas mixture. Repeat the analysis on two additional samples. Measure the peak areas in the three samples and if they do not agree to within 5 percent, analyze additional samples. Record the data. After consistent results are obtained, remove the probe from the source and analyze a second calibration gas mixture. Record this calibration data and the other required data on the data sheet shown in Figure 14, deleting the dilution gas information.

In addition, reanalyze the field audit samples by connecting the audit sample cylinders to the gas sampling valve. Use the same instrument conditions as were used for the source samples. Record the data and report the results of these reanalyses to the audit supervisor.

2.4.4 Dilution Interface Sampling

The sampling of sources containing a high concentration of organic materials will require dilution of the source gas so that the GC detector will not become saturated. The apparatus required for this direct interface procedure is basically the same as that described in the previous section, except that a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

The equipment required in addition to that specified for the direct interface system is as follows:

Sample pump - leakless Teflon-coated diaphragm-type that can withstand being heated to 120°C and deliver 1.5 liters/minute.

Dilution pumps - two pumps are required such as the Model A-150 Komhyr Teflon positive displacement type delivering 150 cc/minute. As an option, calibrated flow meters could be used in conjunction with Teflon-coated diaphragm pumps.

Valves - two valves of a three-way Teflon type suitable for connecting to 6.4-mm-OD Teflon tubing.

Flow meters - two flow meters for measurement of diluent gas, expected delivery flow rate to be 1350 cc/min.

Diluent gas - cylinders and regulators of the diluent gas are required. Gas can be nitrogen or clean dry air, depending on the nature of the source gases.

Heated box - a box suitable for being heated to 120°C is required to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to permit connection of: (1) the heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 16.

The heated box shown in Figure 16 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, the probe heaters are completely eliminated. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on the chromatograph.

The procedure for sampling and analysis using the dilution interface system is as follows:

Assemble the apparatus by connecting the heated box, shown in Figure 16, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple at the centroid of the duct. Measure the source temperature and adjust all heating units to a temperature 0-3°C above this temperature. If this

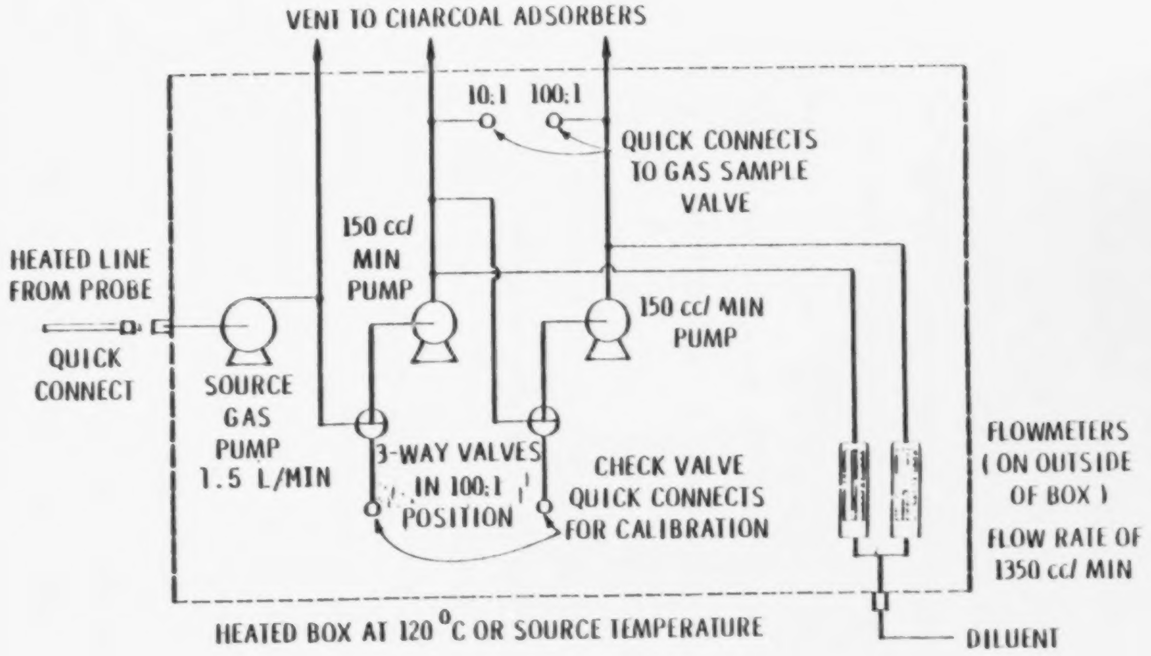

VENT TO CHARCOAL ADSORBERS
10:1
100:1
QUICK CONNECTS TO GAS SAMPLE VALVE
HEATED LINE FROM PROBE
QUICK CONNECT
150 cc/ MIN PUMP
150 cc/ MIN PUMP
SOURCE GAS PUMP 1.5 L/MIN
3-WAY VALVES IN 100:1 POSITION
CHECK VALVE QUICK CONNECTS FOR CALIBRATION
FLOWMETERS (ON OUTSIDE OF BOX)
FLOW RATE OF 1350 cc/ MIN
HEATED BOX AT 120 °C OR SOURCE TEMPERATURE
DILUENT

Figure 16. Schematic diagram of the heated box required for dilution of sample gas.

temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and/or organic compounds. Verify the operation of the dilution system by analyzing a high concentration gas of known composition through either the 10:1 or 100:1 dilution stages, as appropriate. (If necessary, vary the flow of the diluent gas to obtain other dilution ratios.) Determine the concentration of the diluted calibration gas using the dilution factor and the calibration curves prepared in the laboratory. Record the pertinent data on the data sheet shown in Figure 14. If the data on the diluted calibration gas are not within 5 percent of the expected values, it will be necessary to determine whether the chromatograph or the dilution system is in error. Verify the GC operation using a low concentration standard by diverting the gas into the sample loop, bypassing the dilution system. If these analyses are within acceptable limits, the dilution system must be corrected to provide the desired dilution factors. This correction is made using a high-concentration standard gas mixture.

Once the dilution system and GC operation are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards. Analyze three separate samples. If the analyses do not agree withint the accepted limits, collect and analyze additional samples.

Repeat the analysis of the calibration gas mixtures to verify equipment operation. Analyze the two field audit samples using either the dilution gas or direct connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

2.4.5 Modified Procedures Using a Bag Collected Sample

In the event that condensation is observed in the bag collected sample and a direct interface system cannot be used, heat the bag during collection and maintain it at a suitably elevated temperature during all subsequent operations. As an alternate, collect the sample gas and simultaneously dilute it in the Tedlar bag.

In the first procedure, the box containing the sample bag is heated to the source temperature, provided the components of the bag and the surrounding box can withstand this temperature. The bag is then transported as rapidly as possible to the analytical area while maintaining the heating, or by covering the box with an insulating blanket. In the analytical area, the box is kept heated to source temperature until analysis. The method of heating the box and the control for the heating circuit must be compatible with the safety restrictions required in each area. In many cases, the restrictions that prohibit the use of the FID may also eliminate electrical heating elements.

The second procedure involves pre-filling the Tedlar bag with a known quantity of inert gas. The inert gas is metered into the bag by following the procedure for the preparation of gas concentration standards of volatile liquid materials, but eliminating the midget impinger section. This partly filled bag is taken to the source and the source gas is metered into the bag through heated sampling lines and a heated flow meter or Teflon positive displacement pump. The dilution factors should be periodically verified by using known concentration gases.

2.4.6 Reporting of Results

At the completion of the field analysis portion of the study, the data sheets shown in Figure 14 must have been completed. Summarize this data on the data sheets shown in Figure 17.

All data indicated on the table shown in this figure must be filled in. The team leader or other person with the responsibility of determining the validity of the data must sign the data sheets. The signing of the data sheets will confirm that (1) the data was obtained as specified in the manual, (2) any deviations must be specified and (3) the analysis of the audit samples was conducted as required by the audit sample specification (Supplement I-B).

The general information portion is filled out for each bag sample or direct interface sample collected at a site. If the source gas was collected using the bag sampling method, the data on each bag sample must be averaged for the component analysis section. If the direct interface method was used, then the data from each sample analyzed must be separately summarized.

Additional sheets of this page are used for additional compounds. The results of the audit sample analyses are presented on page 4 of the report data sheet.

Gaseous Organic Sampling and Analysis Check List
(Respond with initials or number as appropriate)

Date

1. Presurvey Data
    - A. Grab sample collected ☐ ________
    - B. Grab sample analyzed for composition ☐ ________
        - Method GC ☐
        - GC/MS ☐
        - Other________________ ☐
    - C. GC-FID analysis performed ☐ ________
2. Laboratory Calibration Data
    - A. Calibration curves prepared ☐ ________
        - Number of components ☐
        - Number of concentrations/ component (3 required)
    - B. Audit samples (optional)
        - Analysis completed ☐
        - Verified for concentration ☐ ________
        - OK obtained for field work ☐ ________
3. Sampling Procedures
    - A. Method
        - Bag sample ☐
        - Direct interface ☐
        - Dilution interface ☐
    - B. Number of samples collected ☐ ________
4. Field Analysis
    - A. Total hydrocarbon analysis performed ☐ ________
    - B. Calibration curve prepared ☐ ________
        - Number of components ☐
        - Number of concentrations per component (3 required) ☐

Figure 17. Report data sheets.

4. Field Analysis (Continued)

C. Audit samples (Required)

Analysis completed ☐ ________

Verified for concentration ☐ ________

OK obtained to proceed ☐ ________

D. Source samples ☐ ________

Number of samples collected ☐

Number of replicates per sample ☐

Agreement on replicates (%) ☐

5. Deviations from Method - Specify

____

____

____

____

____

Figure 17 (continued). Report data sheets.

Gaseous Organic Sampling and Analysis Data

Plant ______________________ Date ______________

Location ______________________________________

	Source Sample 1	Source Sample 2	Source Sample 3
1. General Information			
Source temperature (°C)			
Probe temperature (°C)			
Ambient temperature (°C)			
Atmospheric pressure (mm)			
Source pressure (mm)			
Sampling rate (liter/min.)			
Sample loop volume (ml)			
Sample loop temperature (°C)			
Sample collection time (24-hr basis)			
Column temperature			
Initial (°C)			
Program rate (°C/min)			
Final (°C)			
Carrier gas flow rate (ml/min			
Detector temperature (°C)			
Chart speed (inches/min.)			
Dilution gas flow rate (ml/min.)			
Diluent gas used (symbol)			
Dilution ratio			

Performed by (signature): ______________

Date: ______________

Figure 17 (continued). Report data sheets.

Gaseous Organic Sampling and Analysis Data

2. Component Analysis

	Calibration Mixture			Source Sample		
	1	2	3	1	2	3
Component ____________						
Retention time (min.)						
Attenuation factor						
Peak height (mm)						
Peak area (mm^2)						
Area x attenuation (mm^2)						
Dilution factor						
Concentration (ppm)						
Component ____________						
Retention time (min.)						
Attenuation factor						
Peak height (mm)						
Peak area (mm^2)						
Area x attenuation (mm^2)						
Dilution factor						
Concentration (ppm)						
Component ____________						
Retention time (min.)						
Attenuation factor						
Peak height (mm)						
Peak area (mm^2)						
Area x attenuation (mm^2)						
Dilution factor						
Concentration (ppm)						

Performed by (signature): ____________

Date: ____________

Figure 17 (continued). Report data sheets.

Gaseous Organic Sampling and Analysis Data

3. Audit Samples	Audit Sample 1	Audit Sample 2	Audit Sample 3
Retention time (min.)			
Attenuation factor			
Peak height (mm)			
Peak **area** (mm^2)			
Peak area x attenuation factor			
Measured concentration (ppm)			
Data reported on (date)			
Data reported by (initials)			
Certified concentration (ppm)			
Deviation (%)			

Performed by (signature):____________________

Date:____________________

Figure 17 (continued). Report data sheets.

2.5 TOTAL VOLATILE ORGANIC MASS CONTENT OF THE SOURCE GAS

This method is expected to provide information on approximately 90 percent of the total organic mass content of the source emissions. To verify this (has been accomplished), an approximate total organic mass measurement of the source gas must be made with an FID. A second approach is to examine the source gas chromatograms. If there is no more than a trace of unidentified compounds, it may be assumed that 90 percent by mass of the organic components have been measured. The major problem with these two approaches is that the detector or column may not be suitable for revealing additional organic materials. In either event, engineering judgment must be exercised to decide whether undetected organic compounds possibly exist in the stream being studied.

The referee approach is to obtain a total organic mass analysis by GC/MS.

The total FID response data is expressed in terms of propane or carbon equivalents. Standard samples of propane in nitrogen (or air) are used to calibrate the instrument. For this type of study, commercial propane standard gas mixtures will provide the required accuracy. In order to relate the source gas data to the total FID response data, it is necessary to know the composition of the source gas and the relative FID response of each of the components. Approximate values can be obtained from literature sources. However, since response values do vary between individual detectors, more precise values can be found for the detector in use by measuring the response of known concentrations of the components of the source gas relative to propane. A comparison of the total FID response of the source gas (as propane) and the concentration of the identified compounds, each referenced to propane, is then used to determine whether 90 percent of the source gas components have been identified and quantified.

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SUPPLEMENT I-A TO ATTACHMENT I

COLUMN SELECTION

The success or failure of any GC analysis depends on the suitability of the column employed. To effect an adequate chromatographic separation, it is necessary to choose a stationary phase whose separation characteristics closely parallel the nature of the samples to be analyzed. Three basic types of stationary phases possess the capability of adequately separating the classes of compounds commonly encountered in sampling stack gas emissions.

LIQUID PHASE DEPOSITED ON A SOLID SUPPORT

The selection of a suitable solid support requires several considerations. The solid support must have a large surface area and a high porosity, and must be chemically and physically inert, mechanically resistant, and thermally stable at the anticipated operating temperatures. The corresponding liquid stationary phase must also be carefully chosen for efficient separation. Numerous types of liquid phases are commercially available in a broad range of polarities; hydrogen-bonding and several special-purpose phases are available also. The liquid phase selected should have sufficient resolving capabilities for the components to be analyzed, should be fairly selective for the compounds to be encountered, and must be stable on the support at the expected operating temperatures (column bleeding should be minimal).

Liquid phases are manufactured under a variety of trade names, and a survey of any recent chromatographic supplies catalog provides several options suitable to achieve a desired separation. Most liquid phases are relatively limited in the range of compounds they can effectively separate, however, and most complex mixtures require that two or more stationary phases be employed to yield complete and efficient separation. Table A-1 presents a selected listing of liquid phases, their separation capabilities, and their optimum operating temperature ranges.

In addition to the liquid phases shown in Table A-1, the Dexsi® series of liquid phases is sufficiently effective in the general-purpose analysis of high temperature compounds to warrant further discussion.

DEXSIL®

The Olin Corporation's Dexsil High Temperature GC phases are among the most useful of the high-temperature GC column packings available. The structures of this series of three polymeric packings consist of meta-carborane units connected by siloxane units, giving unique separating capabilities. All three polymeric phases are soluble in ether, dichloromethane, chloroform, and aromatic solvents; insoluble in water and alcohols; and stable to most chemicals with the exception of strong bases.

TABLE A-1. COMMONLY EMPLOYED LIQUID STATIONARY PHASES

Liquid phase	Common applications	Optimum operating temperature, °C
Squalane	Saturated hydrocarbons,	0-150
Apiezon L Grease (high molecular weight aliphatic HC)	High boiling point hydrocarbons, especially aromatic compounds	50-300
SE-30 silicone gum rubber	Nonpolar general purpose column; steroids, fatty acid esters, polycyclic aromatic compounds	50-400
DC-200 and DC-500 silicone oils	Intermediate polarity phase for general purpose analysis of aromatic hydrocarbons	20-250
Carbowax 1540 (polyethylene glycol)	Polar compounds such as alcohols, aldehydes, and ketones, etc.	50-200
Carbowax 20M (polypropylene glycol)	High boiling point polar compounds, halogenated compounds, phenols, ethers	60-250
Versamid 900 (polyamide resin)	High boiling point amino compounds	175-300

DEXSIL 300 GC

Dexsil 300 GC, a carborane/methyl silicone polymer, provides effective separation for most organic compounds. Dexsil 300 GC exhibits extremely low bleed characteristics and is the most thermally stable (maximum operating temperature, 450°C) of the stationary phases, adequately separating mixtures of components at high operating temperatures. It is the least polar of this low polarity series.

DEXSIL 400 GC

Dexsil 400 GC, a carborane/methyl phenyl silicone polymer, is only slightly more polar and less viscous than Dexsil 300 GC. Dexsil 400 GC (maximum operating temperature, 375°C) is more efficient in general separations than Dexsil 300 GC, and it is relatively stable over long periods of time. Dexsil 400 GC provides particularly effective separation for mixtures of polynuclear aromatic compounds, and for compounds containing secondary amine groups.

DEXSIL 410 GC

Dexsil 410 GC, a carborane/methyl cyanoethyl silicone polymer, is the most polar of the stationary phases. The 2-cyanoethyl group in the polymer provides unique selectivities for high-temperature (maximum operating temperature, 360°C) separations of compounds containing pi electrons, such as esters, ketones, and the aeromatic compounds.

SOLID STATIONARY PHASE

The solid stationary phase is the second type commonly employed in GC analysis. Columns prepared with solid adsorbing stationary phase packings require no liquid phase and give good chromatographic separations of gases and relatively small organic modules. Several types of solid adsorbents are available commercially; the separation characteristics of a few of these solid phases are delineated in Table A-2.

POROUS POLYMER RESINS

The third principal type of stationary phase employed in the definitive analysis of stack gas emissions is the porous polymer resin. the porous polymers can be used directly in GC columns with no liquid chromatographic phase required. Porous polymer resins are available commercially in a wide variety of polarities and with several different functional groups incorporated in the various copyolymer units. These unique characteristics provide efficient separations for several diverse classes of compounds. With so many of these different polymer options available, it is difficult to present a generalized list of their separation capabilities. Instead, an abbreviated discussion delineating the major applications of a few of the more commonly employed polymeric resins follows.

TABLE A-2. COMMONLY EMPLOYED SOLID STATIONARY PHASES

Solid phase	General composition	Separation capabilities
Carbonaceous phases	Activated carbon	Permanent gases, low boiling point hydrocarbons
Alumina	Alumina	High molecular weight hydrocarbons
Silica gel	Silica	Permanent gases, light hydrocarbons
Molecular sieves	Synthetic zeolites (sodium or calcium silicates)	Inert gases, methane, carbon monoxide
Carbon molecular sieves	Carbonized molecular sieves	Permanent gases, C_1 to C_3 hydrocarbons

PORAPAK®

Porapak is the register trademark for a series of porous polymer resins manufactured by Waters Associates, Inc. These resins are available in eight different types identified, in order of increasing polarity, as P, P-S, Q, Q-S, R, S, N, and T. The first six Porapak resins have a maximum operating temperature of 250°C; Porapak N and T have a maximum operating temperature of 190°C.

PORAPAK P--

Porapak P, the least polar of the series, is a styrene-divinylbenzene copolymer used to separate a wide variety of carbonyl compounds, glycols, and alcohols.

PORAPAK P-S--

Porapak P-S is the surface-silanized version of Porapak P, which minimizes tailing. Its primary applications are in the analysis of aldehydes and glycols.

PORAPAK Q--

Porapak Q, an ethylvinylbenzene-divinylbenzene polymer, the most versatile and commonly employed resin in the series, is particularly effective in the separation of hydrocarbons, organic compounds in water, and oxides of nitrogen.

PORAPAK Q-S--

Porapak Q-S is the surface-silanized version of Porapak Q, which eliminates tailing. It is commonly used to separate organic acids and other polar compounds.

PORAPAK R--

Porapak R, a vinyl pyrollidone polymer of moderate polarity, is employed in the chromatographic analysis of ethers and esters, and in the separation of water from Cl_2 and HCl.

PORAPAK S--

Porapak S, a vinyl pyridine polymer, is applied primarily to the separation of normal and branched chain alcohols.

PORAPAK N--

Porapak N, another vinyl pyrollidone resin, is utilized in the separation of CO_2, NH_3, and H_2O, and in separating acetylene from other C_2 hydrocarbons. This particular resin possesses a high capacity for water retention.

PORAPAK T--

Porapak T, an ethylene glycol-dimethacrylate polymeric resin, exhibits the greatest polarity and the highest water retention capability in the series. It is used primarily in the determination of formaldehyde in aqueous solutions.

CHROMOSORB® CENTURY SERIES

The Chromosorb Century Series, manufactured commercially by Johns-Manville, is available in a series of eight porous polymer resins. All resins in the series are designed for a maximum operating temperature of 250°C.

CHROMOSORB 101--

Chromosorb 101, a styrene-divinylbenzene polymer, is particularly effective in the separation of hydrocarbons, alcohols, fatty acids, esters, aldehydes, ketones, ethers, and glycols. Due to its surface characteristics, Chromosorb 101 eliminates tailing with oxygenated compounds, especially hydroxyl compounds (alcohols, glycols, phenols) and carboxylic acids.

CHROMOSORB 102--

Chromosorb 102, another styrene-divinylbenzene polymer, has an extremely high surface area, causing its behavior to resemble that of a conventional column possessing a high liquid phase loading, and a resulting in relatively long column retention times. It is used in the separation of light and permanent gases, as well as in the analysis of low molecular weight compounds; i.e., acids, alcohols, esters, glycols, ketones, hydrocarbons, etc.

CHROMOSORB 103--

Chromosorb 103, a crosslinked polystyrene polymer, yields fast and efficient analysis of basic compounds such as amines. This resin is also employed in the separation of a wide variety of of compounds including alcohols, aldehydes, hydrazines, amides, and ketones. Gylcols will be completely adsorbed by the resin, and some tailing of water will occur at operating temperatures below 150C.

CHROMOSORB 104--

Chromosorb 104, an acrylonitrile-divinylbenzene polymer, possesses the highest polarity in the Century series. Chromosorb 104 is a multipurpose resin, particularly effective in the separation of nitriles, nitroparaffins, aqueous hydrogen sulfide, xylenols, ammonia, oxides of nitrogen, sulfur, and carbon.

CHROMOSORB 105--

Chromosorb 105, a polyaromatic polymer, is employed primarily for the separation of formaldehyde from water and methanol, the isolation of acetylene from lower hydrocarbon compounds, and the separation of most other organic compounds possessing different polarities and boiling points less than 200°C.

CHROMOSORB 106--

Chromosorb 106, a crosslinked polystyrene polymer, has its primary utility in the retention of benzene and nonpolar organic compounds in relation to polar compounds, and in the separation of C_2 to C_5 fatty acids from the corresponding alcohols.

CHROMOSORB 107--

Chromosorb 107, a crosslinked acrylic ester polymer, is a resin of intermediate polarity. It is a good general purpose column packing, especially efficient in the separation of formaldehyde.

and inorganic gases and volatile organic compounds. XAD-1, XAD-2, and XAD-4 are all crosslinked polystyrene-divinylbenzene copolymers of varying mesh sizes. These nonpolar resins have been used to successfully separate many organic compounds, including phenol, substituted chlorophenols, fatty acids, and amino acids. They also provide adequate separation of permanent and inert gases.

XAD-7 and XAD-8, crosslinked acrylic ester polymeric resins of intermediate polarity, can be applied in the analysis of many permanent gases, C_1 to C_7 alcohols, and volatile organic compounds.

XAD-9, a sulfoxide, XAD-11, an amide, and XAD-12, another very polar material, are utilized primarily in the separation of highly polar compounds.

CHROMOSORB 108--

Chromosorb 108, another crosslinked acrylic ester polymer, is generally applied to the separation of gases and polar materials, such as water, alcohols, aldehydes, ketones, glycols, etc.

TENAX-GC®

Tenax-GC, registered trademark of Tenax B.V., Arnhem, The Netherlands, and commercially available in the U.S., is a porous polymer column packing material based on 2,6-dipenyl-p-phenylene oxide. Tenax-GC exhibits a lower polarity than any of the porous polymers in the Porapak or Chromosorb Century series; compared to these resins, Tenax-GC provides comparable separation of polar compounds with relatively shorter retention times at lower operating temperatures. Two outstanding features of Tenax-GC are its maximum operating temperature of 375°C and very stable baseline after only a short conditioning period.

Tenax-GC has been shown to successfully separate a wide variety of polar high-boiling compounds including alkyl halides, nitroanilines, alcohols, aldehydes, amides, monoamines, diamines, diols, ethanol amines, ketones, methyl esters of dicarboxylic acids, phenols, and polyethylene glycol compounds.

XAD® RESINS

The XAD resins, manufactured by Rohm and Haas, are a series of macroporous cation exchange polymeric resins with well characterized properties for the gas chromatographic separations of organic

SUPPLEMENT I-B TO ATTACHMENT I

DETERMINATION OF ADEQUATE CHROMATOGRAPHIC PEAK RESOLUTION

In this method of dealing with resolution, the extent to which one chromatographic peak overlaps another is determined.

For convenience, consider the range of the elution curve of each compound as running from $-2\sigma_s$ to $+2\sigma$. This range is used in other resolution criteria, and it contains 95.45 percent of the area of a normal curve. If two peaks are separated by a known distance, b, one can determine the fraction of the area of one curve that lies within the range of the other. The extent to which the elution curve of a contaminant compounds overlaps the curve of a compound that is under analysis is found by integrating the contaminant curve over the limits $b-2\sigma_s$ to $b+2\sigma_s$, where σ_s is the standard deviation of the sample curve.

There are several ways this calculation can be simplified. Overlap can be determined for curves of unit area and then actual areas can be introduced. The desired integration can be resolved into two integrals of the normal distribution function for which there are convenient calculation programs and tables. An example would be Program 15 in Texas Instruments Program Manual ST1, 1975, Texas Instruments Inc., Dallas, Texas 75222.

$$\frac{1}{\sqrt{2\pi}\,\sigma_c}\int_{b-2\sigma_s}^{b+2\sigma_s} e^{-\frac{t_c^2}{2\sigma_c}}\,dt = \frac{1}{\sqrt{2\pi}}\int_{\frac{b-2\sigma_s}{\sigma_c}}^{\infty} e^{-\frac{x^2}{2}}\,dx - \frac{1}{\sqrt{2\pi}}\int_{\frac{b+2\sigma_s}{\sigma_c}}^{\infty} e^{-\frac{x^2}{2}}\,dx.$$

The following calculation steps are required:*

1. $2\sigma_s = t_s/\sqrt{2 \ln 2}$

2. $\sigma_c = t_c/2\sqrt{2 \ln 2}$

3. $x_1 = (b-2\sigma_s)/\sigma_c$

4. $x_2 = (b+2\sigma_s)/\sigma_c$

5. $Q(x_1) = \frac{1}{\sqrt{2\pi}} \int_{x_1}^{\infty} e^{-\frac{x^2}{2}} dx$

6. $Q(x_2) = \frac{1}{\sqrt{2\pi}} \int_{x_2}^{\infty} e^{-\frac{x^2}{2}} dx$

7. $I_o = Q(x_1) - Q(x_2)$.

8. $A_o = I_o A_c/A_s$

9. % overlap = $A_o \times 100$

* (Note: In most instances, $Q(x_2)$ is very small and may be neglected.)

Where:

A_s = The area of the sample peak of interest determined by electronic integration, or by the formula $A_s = h_s t_s$.

A_c = The area of the contaminant peak, determined in the same manner as A_s.

b = The distance on the chromatographic chart that separates the maxima of the two peaks.

h_s = The peak height of the sample compound of interest, measured from the average value of the baseline to the maximum of the curve.

t_s = The width of the sample peak of interest at 1/2 of peak height.

t_c = The width of the contaminant peak at 1/2 of peak height.

σ_s = The standard deviation of the sample compound of interest elution curve.

σ_c = The standard deviation of the contaminant elution curve.

$Q(x_1)$ = The integral of the normal distribution function from x_1 to infinity.

$Q(x_2)$ = The integral of the normal distribution function from x_2 to infinity.

I_o = The overlap integral.

A_o = The area overlap fraction.

In judging the suitability of alternate gas chromatographic columns, or the effects of altering chromatographic conditions, one can employ the area overlap as the resolution parameter with a specific maximum permissible value.

The use of Gaussian functions to describe chromatographic elution curves is widespread. However, some elution curves are highly asymetric. In those cases where the sample peak is followed by a contaminant that has a leading edge that rises sharply but the curve then tails off, it may be possible to define an effective width for t_c as "twice the distance from the leading edge to a perpendicular line through the maxim of the contaminant curve, measured along a perpendicular bisection of that line."

SUPPLEMENT I-C TO ATTACHMENT I

PROCEDURE FOR FIELD AUDITING GC ANALYSIS

Responsibilities of audit supervisor and analyst at the source sampling site include the following:

1. To prevent vandalism, check that audit cylinders are stored in a safe location both before and after the audit.

2. At the beginning and conclusion of the audit, record each cylinder number and cylinder pressure. Never analyze an audit cylinder when the pressure drops below 200 psi.

3. During the audit, the analyst is to perform a minimum of two consecutive analyses of each audit cylinder gas. The audit must be conducted to coincide with the analysis of source test samples. Normally, it will be conducted immediately after the GC calibration and prior to the sample analyses.

4. At the end of the audit analyses, the audit supervisor requests the calculated concentrations from the analyst, and then compares the results with the actual audit concentrations. If each measured concentration agrees with the respective actual concentration within ± 10 percent, he then directs the analyst to begin the analysis of source samples. Audit supervisor judgment and/or supervisory policy determines course of action when agreement is not within ± 10 percent. Where a consistent bias in excess of 10 percent is found, it may be possible to proceed with the sample analyses, with a corrective factor to be applied

to the results at a later time. However, every attempt should be made to locate the cause of the discrepancy. The audit supervisor is to record each cylinder number, cylinder pressure (at the end of the audit), and all calculated concentrations. The individual being audited must not under any circumstance be told the actual audit concentrations until the calculated concentrations have been submitted to the audit supervisor.

FIELD AUDIT REPORT

PART A - To be filled out by organization supplying audit cylinders

1. Organization supplying audit sample(s) and shipping address

   ____

2. Audit supervisor, organization, and phone number

   ____

   ____

3. Shipping instructions - Name, Address, Attention

   ____

   ____

   ____

4. Guaranteed arrival date for cylinders ____________________
5. Planned shipping date for cylinders ____________________
6. Details on audit cylinders from last analysis

	Low Conc.	High Conc.
a. Date of last analysis	________	________
b. Cylinder number	________	________
c. Cylinder pressure,	________	________
d. Audit gas(es)/balance gas	________	________
e. Audit gas(es), ppm	________	________
f. Cylinder construction	________	________

PART B - To be filled out by audit supervisor

1. Process sampled______________________________

2. Location of audit______________________________

3. Name of individual audited____________________

4. Audit date ______________________________

5. Audit results

	Low Conc. Cylinder	High Conc. Cylinder
a. Cylinder number	________	________
b. Cylinder pressure before audit, psi	________	________
c. Cylinder pressure after audit, psi	________	________
d. Measured concentration, ppm		
Injection No. 1	________	________
Injection No. 2	________	________
Average[a]	________	________

[a] Results of two consecutive injections that meet the sample analysis criteria of the test method.

f. Audit accuracy[b]

Low Conc. Cylinder ________

High Conc. Cylinder ________

[b] $$\text{Percent accuracy} = \frac{\text{Measured Conc.} - \text{Actual Conc.}}{\text{Actual Conc.}} \times 100$$

g. Problems detected (if any) ______________________________

____

____

____

ATTACHMENT II TO APPENDIX D: DETERMINATION OF THE HEATING VALUE AND VOC EMISSION RATE OF EXHAUST GAS STREAMS

DETERMINATION OF THE HEATING VALUE AND VOC EMISSION RATE OF EXHAUST GAS STREAMS

1. Principle and Applicability

1.1 Principle. This method describes the calculation of the net heating value and VOC emission rate of gas samples. It specifies methods to measure the organic compound content, carbon monoxide content, hydrogen content, and moisture content of the gas sample. These compositional data are used along with published or measured values for the heats of combustion and molecular weights to calculate the heating value and VOC emission rate of the gas sample.

1.2 Applicability. The procedure is applicable to the measurement of the heating value and VOC emission rate of gas streams from synthetic organic chemical manufacturing industries, air oxidation processes.

2. Applicable Procedures

2.1 Measurement of Gaseous Organic Emissions by Gas Chromatography (Appendix D, Attachment I).

2.2 Method 10. Determination of Carbon Monoxide Emissions from Stationary Sources.

2.3 ASTM D 2504-67 (Reapproved 1977). Noncondensable Gases in C_3 and Lighter Hydrocarbon Products by Gas Chromatography.

2.4 ASTM D 2383-76. Standard Test Method for Heat of Combustion of Hydrocarbons by Bomb Calorimeter.

2.5 Method 4. Determination of Moisture Content in Stack Gases.

2.6 Method 2. Determination of Offgas Flowrate.

3. Analysis

3.1 Gas Composition. Determine the molar composition of the gas using the procedures specified in Section 2 above. Measure all components (including water vapor present) in amounts of 10 ppm or greater.

3.2 Heat of Combustion. If any of the components measured in Section 3.1 do not have published heats of combustion, the heat of combustion may be determined experimentally using the procedure in Section 2.4. Alternatively, the heat of combustion may be calculated from the published heats of formation if these are available.

4. Calculation

4.1 Calculate the concentration of the carbon monoxide from Section 2.2 on a wet basis using Equation 1.

$$C_{wco} = C_{co} (1 - B_w) \qquad \text{Eq. 1}$$

where:

C_{wco} = Concentration of carbon monoxide, wet basis, ppm.

C_{co} = Concentration of carbon monoxide from Section 2.2., ppm, dry.

B_w = Water vapor in the gas sample, proportion by volume.

4.2 Calculate the net heating value of the sample gas (25°C, 760 mm) using Equation 2.

$$H_T = K \left(\sum_{i=1}^{n} C_i H_i + C_{wco} H_{co} \right) \qquad \text{Eq. 2}$$

where:

H_T = Net heating value of the sample, MJ/scm, where the net enthalpy per mole of offgas is based on combustion at 25°C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20°C, as in the definition of Q_s (offgas flowrate).

K = Constant, $1.740 \times 10^{-7} \left(\frac{1}{\text{ppm}}\right) \left(\frac{\text{g mole}}{\text{scm}}\right) \left(\frac{\text{MJ}}{\text{kcal}}\right)$, where standard temperature for $\left(\frac{\text{g-mole}}{\text{scm}}\right)$ is 20°C.

C_i = Concentration of sample component i, ppm.

H_i = Net heat of combustion of sample component i, kcal/g-mole. The heats of combustion of process vent stream components would be determined using ASTM D2382-76 if published values are not available or cannot be calculated.

C_{wco} = Concentration of carbon monoxide, wet basis, ppm.

H_{co} = Net heat of combustion of carbon monoxide, kcal/g-mole.

4.3 Calculate the VOC emission rate of the sample gas using Equation 3.

$$E_{VOC} = K \left(\sum_{i=1}^{n} C_i M_i \right) Q_s \qquad \text{Eq. 3}$$

where:

E_{VOC} = VOC emission rate of the sample, kg/hr.

K = Constant, 2.494×10^{-6} (1/ppm) (g-mole/scm) (kg/g) (min/hr), where standard temperature for (g-mole/scm) is 20^{o}C.

M_i = Molecular weight of sample component i, g/g-mole.

Q_s = Vent stream flowrate (scm/min), at a standard temperature of 20^{o}C.

5. Bibliography

5.1 Noncondensable Gases in C_3 and Lighter Hydrocarbon Products by Gas Chromatography. In: 1980 Book of ASTM Standards, Part 24. Philadelphia, Pennsylvania. ASTM Designation D 2504-67. 1980.

5.2 Standard Test Method for Heat of Combustion by Hydrocarbons by Bomb Calorimeter. In: 1980 Book of ASTM Standards, Part 24. Philadelphia, Pennsylvania. ASTM Designation D 2382-76. 1980.

5.3 Perry, J.H. Chemical Engineers Handbook. New York. McGraw-Hill Book Co., Inc. 3rd Edition. 1950. p. 236246.

APPENDIX E: TRE CALCULATIONS

APPENDIX E: TRE CALCULATIONS

E.1 INTRODUCTION

This appendix presents calculations and derivations related to the definition and implementation of regulatory alternatives. Details of the tests and analytical methods involved in the implementation of regulatory alternatives are presented in Appendix D.

E.2 TOTAL RESOURCE-EFFECTIVENESS

Best demonstrated technology (BDT) is based on incineration of certain process vent streams discharged to the atmosphere. The streams for which BDT involves this VOC reduction are those for which the associated total resource-effectiveness (TRE) index value is less than 2.2. Thermal oxidation can reduce VOC emissions by 98 weight percent or to 20 ppm (volume, by compound), whichever is less stringent. An index value of TRE can be associated with each air oxidation vent stream for which the offgas characteristics of flowrate, hourly emissions and net heating value are known. For facilities with a process vent stream or combination of process vent streams having a TRE index value which exceeds the cutoff level of 2.2, the removal of VOC using thermal incineration is not reasonable.

TRE is a measure of the supplemental total resource requirement per unit VOC reduction, associated with VOC control by thermal oxidation. All resources which are expected to be used in VOC control by thermal oxidation are taken into account in the TRE index. The primary resources used are supplemental natural gas, capital, and (for offgas containing halogenated compounds) caustic. Other resources used include labor, electricity, and (for offgas containing halogenated compounds) scrubbing and quench makeup water.

The TRE index is derived from the cost-effectiveness associated with VOC control by thermal oxidation. The calculation of cost-effectiveness and derivation of the TRE index are given in detail in Chapter 5. The total resource-effectiveness (TRE) index of a vent stream is defined as the cost-effectivenesss value of the stream, multiplied by 100, and divided by a cost-effectiveness value of $88.66 thousand/Mg. This value is the cost-effectiveness associated with incineration of that stream in the national statistical profile (described in Appendix F) which is most expensive to control per pound of VOC.* The TRE index is a convenient, dimensionless measure of the total resource burden associated with VOC control at a facility. It is independent of the general inflation rate. However, it does assume fixed relative costs of the various resources, such as carbon steel and natural gas.

The distinction in BDT, between facilities with a TRE index value above the cutoff level and those with a value below it, is meant to encourage the use of product recovery techniques or process modifications to reduce emissions. The values of offgas flowrate, hourly emissions, and net heating value used to calculate the TRE value for a given facility are measured at the outlet of the final piece of product recovery equipment. Use of additional product recovery is expected to decrease VOC emissions and increase the total resource-effectiveness associated with thermal incineration of a vent stream.

The TRE index cutoff level associated with BDT has the value 2.2. The TRE index of a process vent stream is calculated according to the following equation:

$$TRE = \frac{1}{EVOC} \left(a + b\,(Q_s)^{0.88} + c\,(Q_s) + d\,(Q_s)\,(H_T) + e\,(Q_s)^{0.88}\,(H_T)^{0.88} + f\,(H_T)^{0.88}\right)$$

where:

TRE = Total resource-effectiveness index value.

Q_s = Vent stream flowrate (scm/min), at a standard temperature of 20°C.

H_T = Vent stream net heating value (MJ/scm), where the net enthalpy of per mole of offgas is based on combustion at 25°C and 760 mm Hg, but the standard temperature for determining the volume corresponding to one mole is 20°C, as in the definition of Q_s.

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* Excluding four profile vent streams with a reported VOC concentration below the detectable limit.

E_{VOC} = VOC emission rate reported in kg/hr measured at full operating flowrate.

a, b, c, d, e, and f are coefficients. The set of coefficients which apply to a process vent stream can be obtained from Table E-1.

Table E-1 is divided into the six design categories for control equipment. These design categories differ in the amount of heat recovery achieved, in the type of heat recovery equipment used, and in the use of flue gas scrubbing for offgas containing chlorinated compounds. The amount and type of heat recovery used depends upon the offgas heating value. These design categories are defined and discussed in detail in Chapter 5. Under each design category listed in Table E-1, there are several intervals of offgas flowrate. Each flowrate interval is associated with a different set of coefficients. The first flowrate interval in each design category applies to vent streams with a flowrate smaller than that corresponding to the smallest control equipment system easily available without special custom design. The remaining flowrate intervals in each design category apply to vent streams which would be expected to use one, two, three, four, or five sets of control equipment, respectively. These flowrate intervals are distinguished from one another because of limits to prefabricated equipment sizes. The flowrate intervals and maximum offgas flowrate for each design category are presented and discussed in Chapter 8.

An air oxidation vent stream of an affected facility was considered to be "chlorinated" if it contained a concentration of 20 ppmv (by compound) or greater of chlorinated compounds. This low 20 ppmv chlorination cutoff was chosen to avoid control cost and TRE underestimates. Even small amounts of chlorinated compunds may be corrosive, as well as difficult enough to incinerate that a temperature greater than 870°C is necessary to achieve 98 percent control. Therefore, it was judged essential to set a low cutoff, so that control cost and TRE would not be underestimated for any facility. Because the ethylene dichloride process may have affected facilities subject to the proposed standards, the chlorination cutoff was set at 10 percent of the lowest known total chlorinated compound concentration for any existing ethylene dichloride facility, or 20 ppmv.

TABLE E-1. COEFFICIENTS OF THE TOTAL RESOURCE EFFECTIVENESS (TRE) INDEX EQUATION

A1. FOR CHLORINATED PROCESS VENT STREAMS, IF 0 ≤ NET HEATING VALUE (MJ/Nm^3) ≤ 3.5:

W = Design Standard Flowrate (Nm^3/min)	a	b	c	d	e	f
W < 14	45.68	0	0.369	-0.0906	0	0
14 < W ≤ 740	38.04	0.749	0.369	-0.0906	0	0
740 < W ≤ 1480	76.09	0.815	0.369	-0.0906	0	0
1480 < W ≤ 2220	114.13	0.853	0.369	-0.0906	0	0
2220 < W ≤ 2950	152.17	0.885	0.369	-0.0906	0	0
2950 < W ≤ 3690	190.21	0.909	0.369	-0.0906	0	0

A2. FOR CHLORINATED PROCESS VENT STREAMS, IF 3.5 > NET HEATING VALUE (MJ/Nm^3):

W = Design Standard Flowrate (Nm^3/min)	a	b	c	d	e	f
W < 14	45.68	0	-0.0418	0	0	0
14 < W ≤ 740	38.04	0.749	-0.0418	0	0	0
740 < W ≤ 1480	76.09	0.815	-0.0418	0	0	0
1480 < W ≤ 2220	114.13	0.853	-0.0418	0	0	0
2220 < W ≤ 2950	152.17	0.885	-0.0418	0	0	0
2950 < W ≤ 3690	190.21	0.909	-0.0418	0	0	0

B. FOR NONCHLORINATED PROCESS VENT STREAMS, IF 0 ≤ NET HEATING VALUE (MJ/Nm^3) ≤ 0.48:

W = Design Standard Flowrate (Nm^3/min)	a	b	c	d	e	f
W < 14	16.10	0	0.0697	-0.118	0	0
14 < W ≤ 1420	13.78	0.227	0.0697	-0.118	0	0
1420 < W ≤ 2840	27.57	0.247	0.0697	-0.118	0	0
2840 < W ≤ 4260	41.35	0.252	0.0697	-0.118	0	0

C. FOR NONCHLORINATED PROCESS VENT STREAMS, IF 0.48 < NET HEATING VALUE (MJ/Nm^3) ≤ 1.9:

W = Design Standard Flowrate (Nm^3/min)	a	b	c	d	e	f
W < 14	16.27	0	0.240	-0.112	0	0
14 < W ≤ 1420	15.01	0.123	0.240	-0.112	0	0
1420 < W ≤ 2840	30.03	0.134	0.240	-0.112	0	0
2840 < W ≤ 4260	45.04	0.140	0.240	-0.112	0	0

D. FOR NONCHLORINATED PROCESS VENT STREAMS, IF 1.9 < NET HEATING VALUE (MJ/Nm^3) ≤ 3.6:

W = Design Standard Flowrate (Nm^3/min)	a	b	c	d	e	f
W < 14	13.54	0	0.021	0	0	0
14 < W ≤ 1250	11.98	0.153	0.021	0	0	0
1250 < W ≤ 2500	23.96	0.166	0.021	0	0	0
2500 < W ≤ 3750	35.94	0.175	0.021	0	0	0

E. FOR NONCHLORINATED PROCESS VENT STREAMS, IF 3.6 < NET HEATING VALUE (MJ/Nm^3):

W = Design Standard Flowrate (Nm^3/min)	a	b	c	d	e	f
W < 14	13.54	0	0	0.0059	0	0.505
14 < W ≤ 1250	11.98	0	0	0.0059	0.0495	0
1250 < W ≤ 2500	23.96	0	0	0.0059	0.0540	0
2500 < W ≤ 3750	35.94	0	0	0.0059	0.0564	0

E.2.1 Derivation of the TRE Coefficients

The Total Resource Effectiveness (TRE) of an offgas stream is defined as the cost effectiveness of incinerating the VOC stream under consideration divided by the cost effectiveness of incinerating a reference stream, multiplied by 100. The reference stream is chosen to be that stream in the national profile which proved most expensive to control. The cost effectiveness of treating an offgas stream is determined by developing equations for the various annual cost components of the incineration system. These components include annualized capital costs, supplemental gas costs, labor costs, electricity costs, quench water costs, scrub water costs, neutralization costs, and heat recovery credit. The development of each of the cost component equations is summarized in Table E-2.

The parameters that are used in Table E-2 or are required in the derivation of the TRE equation are defined as follows:

E = uncontrolled VOC emission rate, [kg/hr]
N = number of incinerator units, [-]
Flow = total design offgas flow rate, [Nm^3/min]
f/o = flue gas:offgas flow rate, [-]
H_T = heating value of offgas stream [$10^6 J/Nm^3$]
HRF = heat recovery factor of offgas stream, [$10^6 J/Nm^3$]
ΔP = scrubber pressure drop, [inches H_2O]
G_0, G_1, G_2 = coefficients in the supplemental natural gas equation with units as follows:
  G_0 [$10^6 J/min$]
  G_1 [$10^6 J/Nm^3$]
  G_2 [-]

Substituting the cost expressions of Table E-2 into the TRE equation definition yields the following derivation:

TABLE E-2. MATHEMATICAL FORMULATION OF ANNUAL INCINERATOR COST COMPONENTS

Component	Annualized Cost (10^3\$/yr)
1. Annualized Capital Cost, Taxes, and Maintenance	(number of equipment units) x (escalation factor) x (retrofit correction factor) x (capital recovery factor + taxes and maintenance factor) x (capital cost per unit) $= N \times 1.056 \times 1.625 \times (0.163 + 0.11)$ $\times (C_1 + C_2(\mathrm{Flow}/N/0.95)^{0.88})$
2. Supplemental Natural Gas	(gas price) x (supplemental gas required per minute, per unit) x (number of minutes per year) x (number of units) $= 2.40[\$/10^9 J] \times (G_0 + (0.77 \times \mathrm{Flow}/N) \times$ $(G_1 + G_2 \times H_T))[10^6 J/\mathrm{min}] \times$ $0.5256[10^6 \mathrm{min/yr}] \times N$
3. Labor Cost	(labor wage) x (labor factor per unit) x (number of units) $= 11.10/1000[10^3\$/\mathrm{man\text{-}hr}] \times$ $(\mathrm{labor\ factor})[\mathrm{man\text{-}hr/yr}] \times N$
4. Electricity Cost	(electricity price) x (pressure drop) x (average offgas flow rate) x (flue gas:offgas ratio) x (fan equation conversion factor) x (number of hours per year) ÷ (fan efficiency) $= 0.049/1000[10^3\$/\mathrm{kW\text{-}hr}] \times \Delta P[\mathrm{in\ H_2O}] \times$ $0.77 \times \mathrm{Flow}[\mathrm{Nm^3/min}] \times f/o[-] \times$ $0.004136[\mathrm{kW/Nm^3\text{-}in\ H_2O}] \times 8760[\mathrm{hr/yr}] \div 0.6$ $= (0.0604) \times (\$.049) \times \Delta P \times 0.77 \times \mathrm{Flow} \times f/o$

TABLE E-2. (CONTINUED) MATHEMATICAL FORMULATION OF ANNUAL INCINERATOR COST COMPONENTS

Component	Annualized Cost (10^3\$/yr)
5. Quench Water Cost	(water cost) x (average offgas flow rate) x (flue gas:offgas ratio) x (water required per unit flue gas flow rate) x (number of minutes per year) $= \$0.79[\$/10^3 \text{gal}] \times 0.77 \times \text{Flow}[\text{Nm}^3/\text{min}] \times$ $\text{f/o}[-] \times 1.68 \times 10^{-5}[10^3 \text{gal}/\text{Nm}^3] \times 0.5256$ $\times 10^6[\text{min/yr}] \times 1/1000[10^3\$/\$]$ $= \$0.79 \times (0.77 \times \text{Flow}) \times \text{f/o} \times 0.00883$
6. Scrub Water Cost	(water cost) x (average offgas flow rate) x (flue gas:offgas ratio) x (chlorine content of flue gas) x (water required per unit chlorine) x (number of hours per year) $= 0.79[\$/10^3 \text{gal}] \times 0.77 \times \text{Flow}[\text{Nm}^3/\text{min}]$ $\times 35.314 \text{scf}/\text{Nm}^3 \times \text{f/o}[-] \times$ $0.0487\left[\frac{\text{lb/hr chlorine}}{\text{scf/min flue gas}}\right]$ $\times 0.0192[10^3 \text{gal/lb chlorine}]$ $\times 8760 \text{ hr/yr} \times 1/1000[10^3\$/\$]$ $= (\$0.79) \times (0.77 \times \text{Flow}) \times \text{f/o} \times (0.289)$

TABLE E-2. (CONTINUED) MATHEMATICAL FORMULATION OF ANNUAL INCINERATOR COST COMPONENTS

Component	Annualized Cost (10^3\$/yr)
7. Neutralization Cost	(caustic cost) x (average offgas flow rate) x (flue gas: offgas ratio) x (chlorine content of flue gas) x (caustic requirement per unit chlorine) x (number of hours per year) $= \$0.0563[\$/\text{lb NaOH}] \times 0.77 \times \text{Flow}[\text{Nm}^3/\text{min}]$ $\times\ 35.314\ \text{scf/Nm}^3 \times \text{f/o}[-]$ $\times\ 0.0487\left[\frac{\text{lb/hr chlorine}}{\text{scf/min flue gas}}\right]$ $\times\ 1.14[\text{lb NaOH/lb chlorine}] \times 8760[\text{hr/yr}]$ $\times\ 1/1000[10^3\$/\$]$ $= (\$0.0563) \times (0.77 \times \text{Flow}) \times \text{f/o} \times (17.17)$
8. Heat Recovery Credit	(gas price) x (average offgas flow rate) x (energy recovery per unit offgas flow rate) x (number of minutes per year) $= \$2.40[\$/10^9\text{J}] \times 0.77 \times \text{Flow}[\text{Nm}^3\text{min}]$ $\times\ \text{HRF}[10^6\text{J/Nm}^3] \times 0.5256[10^6\text{min/yr}]$ $= (\$2.40) \times (0.77 \times \text{Flow}) \times (0.5256) \times \text{HRF}$

TRE EQUATION DERIVATION

Equation 1:

$$\text{TRE} = \begin{matrix}\text{Total Resource}\\ \text{Effectiveness}\end{matrix} = \frac{\text{cost effectiveness of stream}}{\text{cost effectiveness of reference stream}} \times 100$$

$$= \frac{\text{annualized cost of stream } [10^3\$/\text{yr}] \div \text{emissions reduction } [\text{Mg/yr}]}{55.73 \times 10^3\$/\text{Mg}} \times 100$$

Equation 2:

$$\begin{matrix}\text{annualized cost}\\ \text{of stream } [10^3\$/\text{yr}]\end{matrix} = \left(\begin{matrix}\text{annualized capital}\\ \text{cost}\end{matrix}\right) + \left(\begin{matrix}\text{annual supplemental}\\ \text{gas cost}\end{matrix}\right)$$

$$+ \left(\begin{matrix}\text{annual labor}\\ \text{cost}\end{matrix}\right) + \left(\begin{matrix}\text{annual electricity}\\ \text{cost}\end{matrix}\right)$$

$$+ \left(\begin{matrix}\text{annual quench}\\ \text{water cost}\end{matrix}\right) + \left(\begin{matrix}\text{annual scrub}\\ \text{water cost}\end{matrix}\right)$$

$$+ \left(\begin{matrix}\text{annual neutralization}\\ \text{cost}\end{matrix}\right) - \left(\begin{matrix}\text{annual heat}\\ \text{recovery credit}\end{matrix}\right)$$

$$= N \times 1.056 \times 1.625 \times (0.163 + 0.11)$$

$$\times \left(C_1 + C_2 \left(\frac{\text{Flow}}{N \times 0.95}\right)^{0.88}\right)$$

$$+ \$2.40 \times (G_0 + 0.77 \times \text{Flow} \times (G_1 + G_2 \times H_T))$$

$$\times 0.5256$$

$$+ \$11.10/1000 \times (\text{labor factor})$$

$$+ \$0.049 \times (0.0604) \times \Delta P \times (0.77 \times \text{Flow})$$

$+ \$0.79 \times (0.77 \times \text{Flow}) \times f/o \times (0.00883)$ Category A only

$+ \$0.79 \times (0.77 \times \text{Flow}) \times f/o \times (0.289)$ Category A only

$+ \$0.0563 \times (0.77 \times \text{Flow}) \times f/o \times (17.17)$ Category A only

$- \$2.40 \times (0.77 \times \text{Flow}) \times 0.5256 \times \text{HRF}$ Category A only

Equation 3:

$$\underset{[\text{Mg/yr}]}{\text{emissions reduction}} = \left(\begin{matrix}\text{hourly uncontrolled}\\ \text{emissions}\end{matrix}\right) \times \left(\begin{matrix}\text{number of days}\\ \text{per year}\end{matrix}\right)$$

$$\times \left(\begin{matrix}\text{number of hours}\\ \text{per day}\end{matrix}\right) \times \left(\begin{matrix}\text{capacity}\\ \text{utilization}\end{matrix}\right)$$

$$\times (\text{VOC destruction efficiency})$$

$$= E\,[\text{kg/hr}] \times 10^{-3}[\text{Mg/kg}] \times 365\,[\text{days/year}]$$

$$\times 24\,[\text{hours/day}] \times 0.77 \times 0.98$$

Equation 4:

$$\text{TRE} = \frac{(\text{annualized cost of stream})\,[10^3\$/\text{yr}]}{(55.73)[10^3\$/\text{Mg}] \times E\,[\text{kg/hr}] \times 6.610\,[\frac{\text{Mg-hr}}{\text{kg-yr}}]}$$

$$\times 100 = 0.2714 \times \frac{(\text{annualized cost of stream})[10^3\$/\text{yr}]}{E\,[\text{kg/hr}]}$$

$$= (0.2714/E) \times \{N \times 1.056 \times 1.625 \times (0.163 + 0.11) \times$$

$$(C_1 + C_2\,(\text{flow}/N/0.95)^{0.88}$$

$$+ N \times (2.40 \times (G_o + 0.77 \times \text{Flow}/N \times (G_1 + G_2 \times H_T))$$

$$\times 0.5256) + N \times 11.10/1000 \times (\text{labor factor})$$

$$+ 0.049 \times (0.0604) \times \Delta P \times (0.77 \times \text{flow} \times f/o)$$

$$+ [0.79 \times (0.77 \times \text{Flow}) \times f/o \times (0.00883)$$

$$+ 0.79 \times (0.77 \times \text{Flow}) \times f/o\,(0.289) + 0.00563 \times f/o$$

$$\times (0.77 \times \text{Flow}) \times (17.17)$$

$$- 2.40 \times (0.77 \times \text{Flow}) \times 0.5256 \times \text{HRF}]\}$$

Note: The terms contained in brackets [ ] apply to category A only.

Next, the TRE equation is rearranged in the form:

Equation 5:

$$\text{TRE} = \frac{1}{E}\,(\,a + b(\text{flow})^{0.88} + c(\text{flow}) + d\,(\text{flow})(H_T)$$

$$+ e(\text{flow})^{0.88}\,(H_T)^{0.88} + f(H_T)^{0.88})$$

Coefficients a through f are derived by substituting numeric values for all quantities except flow, H_T, and E, and then collecting like algebraic terms. Design categories B, C, and D always have the same expressions for the coefficients, while design categories A and E must be considered individually for some of the coefficients. Category A has costs associated with chlorine removal that are unique among the design categories. Category E is unique because the offgas flow is diluted prior to incineration such that the variable "flow" is replaced everywhere in Equations 2, 3, and 4 by "flow x $H_T/3.6$." These special features of categories A and E lead to variations in the expressions for coefficients a through f.

The term in the TRE equation involving coefficient a is independent of flow. The expression for coefficient a is identical for all design categories, and it consists of terms involving C1, G_o, and a labor factor. If the operating flow rate is less than 14 Nm^3/min, then the expression also includes a term involving C2 because in this case the fixed value flow = 14 Nm^3/min is used in the annualized capital cost expression.

- For design categories A, B, C, D, and E:
  - when flow <14 Nm^3/min

$$a = 0.2714 \times 1.056 \times 1.625 \times 0.273 \times N \times C1 + 0.2714 \times 2.40 \times 0.5256 \times G_o \times N + N \times 0.0111 \times 0.2714 \times (\text{labor factor}) + 0.2714 \times N \times 1.056 \times 1.625 \times 0.273 \times C2 \times (14/0.95)^{0.88}$$

$$= 0.1271 \times N \times C1 + 0.3424 \times G_o \times N + 0.003 \times N \times (\text{labor factor}) + 0.1271 \times N \times C2 \times (14/0.95)^{0.88}$$

  - when flow >14 Nm^3/min

$$a = 0.2714 \times 1.056 \times 1.625 \times 0.273 \times N \times C1 + 0.2714 \times 2.40 \times 0.5256 \times G_o \times N + N \times 0.111 \times 0.2714 \times (\text{labor factor})$$

$$= 0.1271 \times N \times C1 + 0.3424 \times G_o \times N + 0.003 \times N \times (\text{labor factor})$$

The term in the TRE equation involving coefficient b depends on $(\text{flow})^{0.88}$. For design categories A, B, C, and D, the expression for coefficient b includes just one term that depends on C2, and therefore, coefficient b is non-zero only when coefficient a does not include the C2 term (i.e., coefficient b is non-zero only when flow >14 Nm^3/min). Coefficient b equals zero regardless of the value of flow for category E.

- For design categories A, B, C, and D:
  - when flow <14 Nm^3/min

    $b = 0$
  - when flow >14 Nm^3/min

    $$b = 0.2714 \times N \times 1.056 \times 1.625 \times 0.273 \times C2 \times 0.95^{0.88} \times N^{-0.88}$$
    $$= N^{0.12} \times 0.133 \times C2$$
- For design category E:

  $b = 0$ (all flow values)

The term in the TRE equation involving coefficient c depends on (flow). For design category A, the expression for coefficient c includes terms that depend on G1, ΔP, f/o, (f/o) x (ΔP), and HRF. For design categories B, C, and D, HRF = 0 and the corresponding term does not appear in the expression for c. Coefficient c is zero for design category E.

- For design category A:

  $$c = 0.77[0.2714 \times 2.4 \times 0.5256(G1-HRF) + 0.2714 \times 0.0604 \times 0.049 \times \Delta P \times f/o + 0.2714(0.79 \times 0.00883 + 0.79 \times 0.289 + 0.0563 \times 17.17)\ f/o]$$

  $$= 0.77[0.3424(G1-HRF) + .000803(\Delta P)f/o + 0.327\ f/o]$$
- For design categories B, C, and D:

  $$c = 0.77[0.2714 \times 2.4 \times 0.5256 \times G1 + 0.2714 \times 0.0604 \times 0.049 \times \Delta P \times f/o]$$

  $$= 0.77[0.3424 \times G1 + 0.000803(\Delta P)f/o]$$
- For design category E:

  $c = 0$

The term in the TRE equation involving coefficient d depends on the (flow) x (H_T) product. For design categories A, B, C, and D, the expression for coefficient d consists of just one term that depends on G2. For design category E, the expression for coefficient d consists of terms depending on G1 and the (ΔP) x (f/ρ) product.

- For design categories A, B, C, and D:

$$d = 0.77 \times 0.2714 \times 2.4 \times 0.5256 \times G2$$

$$= 0.77 \times 0.3424 \times G2$$

- For design category E:

$$d = 0.77/3.6 \times 0.2714[2.40 \times 0.5256 \times G1 + 0.049 \times 0.0604 \times \Delta P \times f/\rho]$$

$$= 0.77/3.6[0.3424 \times G1 + 0.000803 \times \Delta P \times f/\rho]$$

The term in the TRE equation involving coefficient e depends on the $(\text{flow})^{0.88} \times (H_T)^{0.88}$ product. This product arises only in the TRE expression for category E.

- For design categories A, B, C, and D:

  e = 0 (all values of flow)

- For design category E:

  - when flow <14 Nm^3/min

    e = 0

  - when flow >14 Nm^3/min

$$e = 0.2714 \times N \times 1.056 \times 1.625 \times 0.273 \times C2 \times 3.6^{-0.88} \times 0.95^{-0.88} \times N^{-0.88}$$

$$= N^{0.12} \times 0.1271 \times C2/3.6^{0.88}/0.95^{0.88}$$

The term in the TRE equation involving coefficient f depends on $(H_T)^{0.88}$. Coefficient f is zero for design categories A, B, C, and D. The value of coefficient f is non-zero only if flow <14 Nm^3/min for design category E.

- For design categories A, B, C, and D:

  f = 0 (all values of flow)

- For design category E

  - when flow <14 Nm^3/min

    $$f = 0.2714 \times 1 \times 1.056 \times 1.625 \times 0.273 \times C2 \times 3.6^{-0.88} \times 0.95^{-0.88} \times 14^{0.88} \times 1^{-0.88}$$

    $$= 0.1271 \times C2 \times 3.6^{-0.88} \times 0.95^{-0.88} \times 14^{0.88}$$

  - when flow >14 Nm^3/min

    f = 0

E.2.2 Example Calculation of the TRE Index Value for a Facility

This section presents an example of use of the TRE index equation for determination of the design category applicable to an individual air oxidation facility. It has been determined that the air oxidation process vent stream has the following characteristics:

1. Q_s = 284 scm/min (10,000 scfm).
2. H_T = 0.37 MJ/scm (10 Btu/scf).
3. Hourly Emissions (E_{VOC}) = 76.1 kg/hr.
4. No chlorinated compounds in the offgas.

Because there are no chlorinated compounds in the offgas, design Category A is not the applicable one. Categories B, C, D, and E all correspond to nonchlorinated vent streams. Because the offgas net heating value is 0.37 scm/min, Category B is the applicable one. The offgas flowrate is 284 scm/min, and therefore the second flowrate interval under Category B is the applicable one. The coefficients for Category B, flow interval #2 are:

1. $a = 15.83$
2. $b = 0.215$
3. $c = 0.240$
4. $d = -0.426$
5. $e = 0$
6. $f = 0$

The TRE equation is:

$$TRE = (1/76.1)(15.83 + 0.215\,(284)^{0.88} + (0.240)(284) - 0.426\,(284)(.37) + 0 + 0)$$

$$TRE = 0.21 + 0.41 + 0.89 - 0.59 + 0 + 0$$

$$TRE = 0.9$$

Since the calculated total resource-effectiveness (TRE) index value of 0.9 is less than the cutoff value of 2.2, the applicable BDT for this facility would be 98 percent VOC reduction or reduction to 20 ppm. If process modifications or increased product recovery were introduced, the product recovery vent offgas percent VOC and heating value might be sufficiently decreased that the resulting TRE value would exceed the 2.2 cutoff.

E.2.3 Calculation of Cost-effectiveness for a Facility

Because the TRE index is a cost-effectiveness ratio, it is possible to calculate cost-effectiveness for any vent stream given its TRE index value. The TRE index value of the facility is divided by 100 (since TRE is a percentage), multiplied by the indexing constant $88.66 thousand/Mg, and finally multiplied by 1000 (to convert the units to $/Mg). For the stream used in the example above, the cost-effectiveness is found as follows:

TRE = 0.9

Indexing constant = $88.66 thousand/Mg

Cost effectiveness = (0.9)(88.66)(1000)/100 = $800/Mg.

APPENDIX F: STATISTICAL ANALYSIS

APPENDIX F: STATISTICAL ANALYSIS

F.1 INTRODUCTION

The purpose of this appendix is to describe the methods of statistical analysis used in the development of the air oxidation unit process new source performance standard (NSPS). The method of regulatory analysis developed for this NSPS uses a national statistical profile, representing the air oxidation segment of SOCMI to project the energy, cost, and environmental impacts associated with VOC control using several regulatory alternatives. A method for statistically estimating offgas flowrates for air oxidation processes is also described.

F.2 STATISTICAL IMPACT ANALYSIS

Typically, an NSPS would be developed on a chemical-by-chemical basis. Because the processes used by a single chemical-producing industry to manufacture a specific product do not differ greatly, it is possible to design a model plant that can be used to represent the emissions and control device requirements of typical new, modified, or reconstructed sources covered in the NSPS. This model, along with projectsions regarding the population of new sources, would be used to determine the environmental, energy, and cost impacts associated with several regulatory alternatives.

Air oxidation facilities, however, use 36 types of oxidation processes (23 principal processes and 13 specialty processes) to manufacture 36 different organic chemicals. Because of the number and diversity of facilities and processes in the air oxidation industry, a chemical-by-chemical development of NSPS's would require large amounts of time, effort, and money. The unit process approach, on the other hand, allows development of an NSPS that provides for regulatory alternative development for VOC emissions from all SOCMI air oxidation processes. This unit process approach allows the resource-efficient statistical estimation of the impacts associated with VOC emissions control from all air oxidation processes under several regulatory alternatives.

In the unit process approach, no model plants are used for impact analysis. Rather, the information concerning existing air oxidation facilities is analyzed statistically and used to construct a national profile. This national profile replaces the traditional model plant and can be considered a statistical model of new SOCMI air oxidation processes and facilities. The national profile characterizes air oxidation processes according to national distributions of key variables (e.g., waste gas stream flow, heating value, and VOC content) that can be used to determine VOC emissions and the cost and energy impacts associated with the regulatory alternatives. Each alternative is therefore recommended as a national percent reduction in annual VOC emissions based on thermal oxidation as the single control technique. The regulatory alternative impacts are evaluated as impacts upon the entire population of affected facilities.

F.2.1 National Statistical Profile Construction

The overall success of the statistical analysis depends on the availability of an adequate sample size and dependable data. Thirty-six chemicals are produced by air oxidation processes nationwide. The results of the EPA Houdry Questionnaires contain data on 13 chemicals. These data consist of emission and production factors for 59 chemical plants, representing 36 percent of the total existing population and 120 percent of the projected new population for 1982-1987. These results, along with the physical properties of the chemicals involved, form the basis of the analysis. Table F-1 lists the chemicals that are included in the data base.

As noted, the data base for NSPS analysis has been derived from EPA Houdry Questionnaires. The Houdry Division of Air Products and Chemicals, Inc., conducted an extensive survey of the petrochemical industry to provide data for EPA to use in their fulfillment of their obligations under the terms of the Clean Air Amendments of 1970. The scope of that study included most petrochemicals which fell into one or more of the classifications of (1) large production, (2) high growth rate, and (3) significant air pollution. The information sought included industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions, and descriptions of emission control devices then in use. The principal source for that data was the industry questionnaire current as of 1972. The data base was updated in 1979.

TABLE F-1. LIST OF CHEMICALS FOR WHICH DATA HAS BEEN OBTAINED

Ethylene Oxide
Hydrogen Cyanide
Acetic Acid
Acetaldehyde
Phthalic Anhydride
Dimethyl Terephthalate
Phenol
Ethylene Dichloride
Acrylonitrile
Cyclohexanone
Terephthalic Acid
Maleic Anhydride
Formaldehyde

TABLE F-2. ACTUAL DATA BASE USED TO CONSTRUCT NATIONAL STATISTICAL PROFILE

Company	Location	Process
Rohm & Haas	Deer Park, TX	Methane/Ammonia Oxidation
Badische	Freeport, TX	Cyclohexane Oxidation
Badische	Freeport, TX	Cyclohexane Oxidation
Nipro	Augusta, GA	Cyclohexane Oxidation
Clark	Blue Island, IL	Cumene Hydroperoxidation
Dow	Oyster Creek, TX	Cumene Hydroperoxidation
Georgia Pacific	Plaquemine, LA	Cumene Hydroperoxidation
Monsanto	Choc. Bayou, TX	Cumene Hydroperoxidation
Shell	Deer Park, TX	Cumene Hydroperoxidation
USS	Haverhill, OH	Cumene Hydroperoxidation
DuPont	Wilmington, NC	DMT p-Xylene Oxidation
DuPont	Old Hickory, TN	DMT p-Xylene Oxidation
Eastman	Kingsport, TN	TPA p-Xylene Oxidation
Amoco/Standard	Decatur, AL	TPA p-Xylene Oxidation
Exxon	Baton Rouge, LA	o-Xylene Oxidation
Monsanto	Texas City, TX	o-Xylene Oxidation
Stepan	Millsdale, IL	o-Xylene Oxidation
Conoco	Covenant, LA	Ethylene Oxychlorination
Diamond Shamrock	Deer Park, TX	Ethylene Oxychlorination
Dow	Freeport, TX	Ethylene Oxychlorination
Ethyl	Baton Rouge, LA	Ethylene Oxychlorination
Goodrich	Calvert City, KY	Ethylene Oxychlorination
ICI	Baton Rouge, LA	Ethylene Oxychlorination
Shell	Deer Park, TX	Ethylene Oxychlorination
Stauffer	Long Beach, CA	Ethylene Oxychlorination
Vulcan	Grismar, LA	Ethylene Oxychlorination
Dow	Freeport, TX	Ethylene Oxidation I

TABLE F-2 (Continued). ACTUAL DATA BASE USED TO CONSTRUCT NATIONAL STATISTICAL PROFILE

Company	Location	Process
Koch	Orange, TX	Ethylene Oxidation I
UCC	Seadrift, TX	Ethylene Oxidation I
PPG	Beaumont, TX	Ethylene Oxidation I
Eastman	Longview, TX	Ethylene Oxidation II
American Cyanamid	New Orleans, LA	Propylene Ammoxidation
DuPont	Beaumont, TX	Propylene Ammoxidation
Monsanto	Alvin, TX	Propylene Ammoxidation
Vistron	Lima, OH	Propylene Ammoxidation
Denka	Houston, TX	Benzene Oxidation
Monsanto	St. Louis, MO	Benzene Oxidation
Koppers	Bridgeville, PA	Benzene Oxidation
Reichhold	Morris, IL	Benzene Oxidation
Reichhold	Elizabeth, NJ	Benzene Oxidation
Tenneco	Fords, NJ	Benzene Oxidation
USS	Neville Island, PA	Benzene Oxidation
USS	Neville Island, PA	Naphthalene Oxidation
UCC	Charleston, WV	Naphthalene Oxidation
Gulf	Vicksburg, MS	Methanol Oxidation I
Reichhold	Houston, TX	Methanol Oxidation I
GAF	Calvert City, KY	Methanol Oxidation I
Reichhold	Moncure, NC	Methanol Oxidation I
Borden	Fayetteville, NC	Methanol Oxidation II
Celanese	Bishop, TX	Methanol Oxidation II
DuPont	Belle, WV	Methanol Oxidation II
Georgia Pacific	Vienna, GA	Methanol Oxidation II
Monsanto	Choc. Bayou, TX	Methanol Oxidation II
Georgia Pacific	Crossett, AR	Methanol Oxidation II

TABLE F-2 (Continued). ACTUAL DATA BASE USED TO CONSTRUCT NATIONAL STATISTICAL PROFILE

Company	Location	Process
Hercules	Wilmington, NC	Methanol Oxidation II
Reichhold	Kansas City, KS	Methanol Oxidation II
Tenneco	Garfield, NJ	Methanol Oxidation II
Eastman	Kingsport, TN	Acetaldehyde Oxidation

Table F-2 shows the actual data base used to construct the national statistical profile. Twenty-three different processes are represented in the data set. Due to the wide variation in processes used and in the types of control devices present across the air oxidation industry, only uncontrolled emission factors and vent stream characteristics are included in the data set. Since uncontrolled emissions are subject to the greatest uncertainty because of the difficulty in defining what is a pollution control device, all stream data represent the process stream exiting the primary product recovery device. Figure F-1 shows the reference point for data collection within the air oxidation process. Since many air oxidation facilities may have additional control equipment in place, these data are overstated estimates of the current emission factors. Table F-3 shows the air oxidation offgas components specific to each chemical represented in the data base VOC. Table F-4 shows the data vectors contained in the national statistical profile. Tables F-5 and F-6 show tabular representations of the vector distribution.

F.2.2 Data Reliability

From the Houdry data, two assumptions must be made regarding the Houdry data reliability for this NSPS analysis. First, the data contains a bias toward large-volume chemicals or those chemicals with significant air pollution. This is not considered to be a serious drawback to the NSPS analysis. Second, because the chemical industry as a whole is dynamic, the age of the Houdry data presented a second source of bias. In a study prepared for the Chemical Manufacturers Association (CMA), the 1972 Houdry data (updated in 1979) was compared to a 1980 data base developed from recent industry contacts. Twenty-two plants are represented in both the CMA data base and the data base used for this NSPS analysis. Hypothetical uncontrolled emission factors were calculated for each data vector representing a plant for which data exists in both data bases. Two sets of 22 emission factors each, one set for each data base, were thereby obtained. These two sets were statistically compared using the Wilcoxon signed-rank procedure. The results of the Wilcoxon signed-rank procedure to test the significance of the differences between the overlapping portions of the two data bases show that the differences are not significant at the 0.05 level.

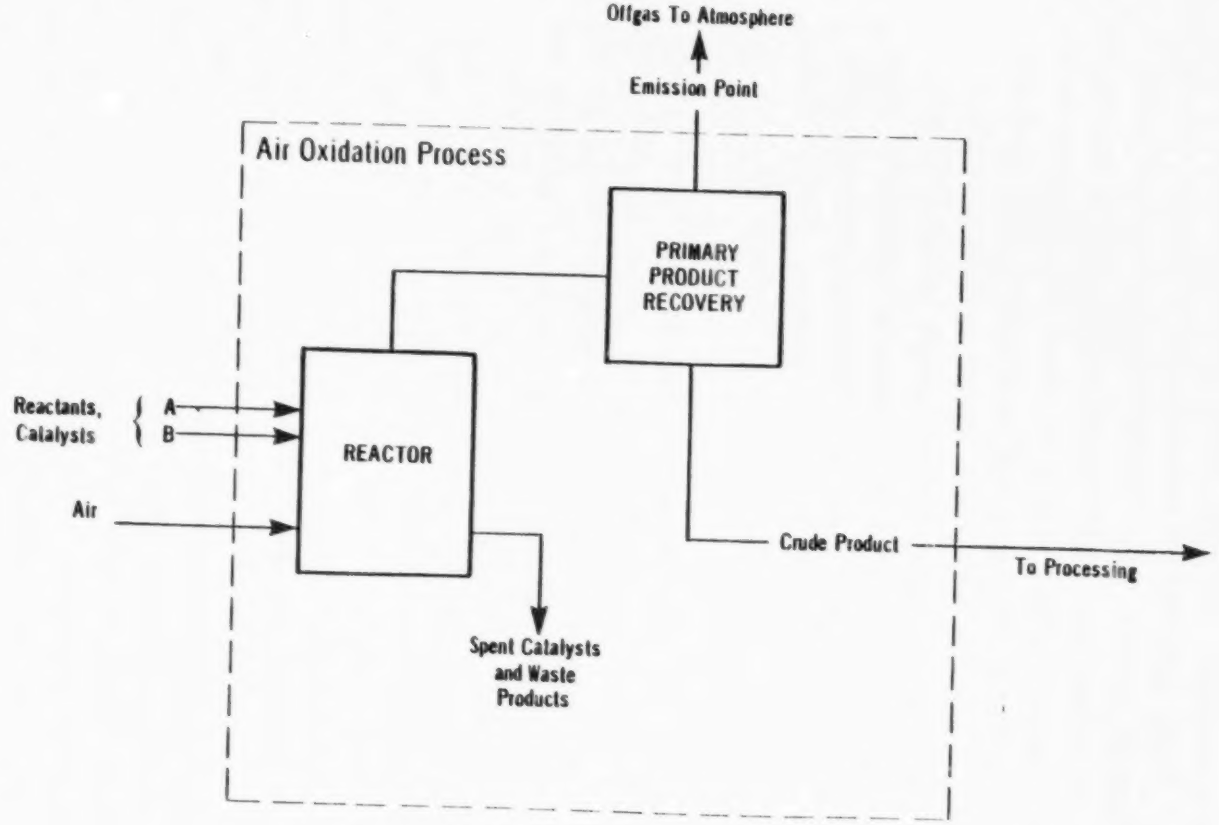
Offgas To Atmosphere
Emission Point
Air Oxidation Process
PRIMARY PRODUCT RECOVERY
Reactants, Catalysts
A
B
REACTOR
Air
Crude Product
To Processing
Spent Catalysts and Waste Products

Figure F-1. General air oxidation process.

TABLE F-3. AIR OXIDATION OFFGAS COMPONENTS

ACRYLONITRILE

Nitrogen
Oxygen
Carbon Dioxide
Carbon Monoxide
Water (vapor)
Ammonia*
Methane
Ethane
Ethylene
Propane
Propylene*
Acetaldehyde
Acetone (vapor)
Acrolein (propenal) (vapor)
Hydrogen Cyanide
Acrylonitrile (vapor)*
Acetonitrile (vapor)

HYDROGEN CYANIDE

"Air"
Hydrogen Cyanide*

CYCLOHEXANONE

Nitrogen
Carbon Monoxide
Cyclohexane (vapor)*
Cyclohexanol (vapor)
Cyclohexanone (vapor)*
"Unknown Organics (C_2^+)"

ACETALDEHYDE

Nitrogen
Oxygen
Carbon Dioxide
Carbon Monoxide
Water (vapor)
Hydrogen
Methane
Methyl Chloride
Ethyl Chloride
Ethanol (vapor)*
Acetic Acid (vapor)
Acetaldehyde (vapor)*
Argon

TABLE F-3 (Continued). AIR OXIDATION OFFGAS COMPONENTS

ACETIC ACID

Nitrogen
Oxygen
Carbon Dioxide
Water (vapor)
Carbon Monoxide*
Argon
Hydrogen
Methane
Ethane
Butane*
"C_2^+ Hydrocarbons"
Methyl Iodide
Ethanol*
Acetaldehyde*
Methyl Acetate
Ethyl Acetate

ACETIC ANHYDRIDE

Nitrogen
Oxygen
Carbon Dioxide
Carbon Monoxide
Hydrogen
Methane
Ethane
Ethylene
Propane
Propadiene
Acetic Acid (vapor)*
Diketene (vapor) "$(CH_2=C=O)_2$"
Acetic Anhydride (vapor)*

MALEIC ANHYDRIDE

Nitrogen
Oxygen
Carbon Dioxide
Water (vapor)
Carbon Monoxide
Formaldehyde
Formic Acid (vapor)
Maleic Acid (vapor)
Maleic Anhydride (vapor*)
Benzene (vapor)*
Xylene (vapor)
"Other Organics (Est. Mol. Wt. 50)"

TABLE F-3 (Continued). AIR OXIDATION OFFGAS COMPONENTS

PHTHALIC ANHYDRIDE

- Nitrogen
- Oxygen
- Water (vapor)
- Carbon Monoxide
- Carbon Dioxide
- Argon
- Sulfur Dioxide*
- Inorganic Salts (Magnesium and Calcium Carbonates) (particulate)
- "Hydrocarbons"
- Maleic Acid (vapor)
- Maleic Anhydride (vapor)
- Benzoic Acid (vapor)
- Phthalic Anhydride*
- 1,2-Naphthoquinone (particulate, vapor)

TEREPHTHALIC ACID & DIMETHYL TEREPHTHALATE

- Nitrogen
- Oxygen
- Water (vapor)
- Carbon Dioxide
- Carbon Monoxide
- Methane
- Methanol*
- Dimethyl Ether
- Methyl Ethyl Ketone (vapor)*
- Methyl Acetate (vapor)
- Acetic Acid (vapor)*
- Acetaldehyde*
- p-Xylene (vapor)*

PHENOL

- Nitrogen
- Oxygen
- Water (vapor)
- Carbon Dioxide
- Sodium Carbonate (particulate)
- Formaldehyde
- Acetaldehyde
- Acetone (vapor)
- Acetone (vapor)
- Mesityl Oxide (4-Methyl-3-Penten-2-One (vapor)
- Benzene (vapor)
- Phenol (vapor)*
- Cumene (vapor)*
- Cumene Hydroperoxide (vapor)
- α-Methyl Styrene (vapor)
- α,α-Dimethyl Benzyl Alcohol (2-Phenyl-2-Propanol) (vapor)
- Acetophenone
- "Other Organics", "Oxidized Organics (various)" (vapor)

ETHYLENE OXIDE

- Nitrogen
- Oxygen
- Carbon Dioxide
- "Oxides of Nitrogen"
- Argon
- Methane
- Ethane
- Ethylene*
- Ethylene Oxide*
- "Particulate (Primarily Carbon, small amounts of Iron, Chlorine)"

*Product or Feedstock

TABLE F-4. DISTRIBUTION OF NATIONAL STATISTICAL PROFILE DATA VECTORS

Plant ID Number	Hourly Emissions (kg/hr)	Net Heating Value (MJ/scm)	Offgas Flowrate (scm/min)
1303	326	0.592	461
1305	566	1.05	529
1306	115	0.499	194
1307	2.12	0.001	3037
1601	55.0	3.31	1631
205	75.0	0.234	152
2301	117	0.140	790
2302	203	0.144	1212
2303	617	0.093	3552
2305	340	0.090	2307
2308	219	0.146	1320
5101	1370	1.04	1427
5102	2150	1.59	1373
5103	395	0.728	1524
5104	1210	0.676	2092
102	13.7	0.009	365
1004	323	0.269	1524
1007	223	0.154	565
2203	155	0.217	516
2204	26.4	0.062	456
2205	27.9	0.065	310
2206	36.0	0.087	231
2207	13.7	0.065	152
2208	14.6	0.109	97
902	80.2	0.440	182
903	103	0.433	182
904	407	1.52	252
1001	78.7	0.366	1642
1005	188	0.143	979
1801	529	0.391	2264
1802	211	0.336	1341
1803	205	0.387	1277
1804	136	0.450	516
1805	14.1	0.205	1309
1806	135	0.335	912
1807	355	0.753	607
1403	15.1	2.63	24
1404	20.3	2.45	73
1407	33.7	2.63	61
1408	14.6	2.54	76
1409	0.0250	2.75	33
1410	15.8	2.53	173
1411	357	2.84	547
1418	0.0205	2.39	27
1416	39.6	0.106	176
1421	16.0	0.138	118
1423	19.5	0.137	118
1422	23.3	0.299	100
1420	31.4	2.57	61
1601	0.217	1.71	197
5202	80.2	0.752	182
5203	433	1.99	121
5204	348	2.65	216
5205	228	2.00	647
5206	125	0.722	143
5207	464	0.769	304
5208	371	0.769	242
5209	78.9	0.769	52
5201	616	4.25	289

TABLE F-5. JOINT DISTRIBUTION OF FLOW AND MASS EMISSIONS IN NATIONAL STATISTICAL PROFILE

Offgas Flow (Q_s) scm/min	Hourly Emissions (E_{VOC}) kg/hr					
	$E_{VOC} \leq 5$	$5 < E_{VOC} \leq 25$	$25 < E_{VOC} \leq 50$	$50 < E_{VOC} \leq 100$	$100 < E_{VOC} \leq 200$	$200 < E_{VOC}$
$Q_s \leq 15$	-	-	-	-	-	-
$15 < Q_s \leq 30$	1	1	3	-	-	-
$30 < Q_s \leq 152$	1	9	2	-	1	1
$152 < Q_s \leq 760$	1	7	3	3	7	1
$760 < Q_s \leq 1524$	-	1	-	6	1	3
$1524 < Q_s$	1	1	1	-	1	3

TABLE F-6. JOINT DISTRIBUTION OF DESIGN CATEGORIES AND MASS EMISSIONS IN NATIONAL STATISTIC PROFILE

Category	Net Heating Value (H_T) MJ/scm	Hourly Emissions (E_{VOC}) kg/hr					
		$E_{VOC} \leq 5$	$5 < E_{VOC} \leq 25$	$25 < E_{VOC} \leq 50$	$50 < E_{VOC} \leq 100$	$100 < E_{VOC} \leq 200$	$200 < E_{VOC}$
A1 (Halogenated)	$0 \leq H_T \leq 3.3$	-	-	3	-	3	1
A2 (Halogenated)	$3.3 < H_T$	-	-	-	-	-	-
B (Not Halogenated)	$0 \leq H_T \leq 0.45$	1	12	6	7	4	6
C (Not Halogenated)	$0.45 \leq H_T \leq 1.8$	3	7	-	2	3	1
D (Not Halogenated)	$1.8 \leq H_T \leq 3.4$	-	-	-	-	-	-
E (Not Halogenated)	$3.4 < H_T$	-	-	-	-	-	-

F.2.3 National Statistical Profile Use

The actual use of the national statistical profile assumes that the distribution of offgas flow, VOC emission rate, and stream net heating value is chemical independent. Chemical identities are not considered in the profile, nor is there claimed to be a one-to-one correspondence between any one data vector and an existing offgas stream. It is assumed, however, that the overall proportions and distributions of the parameter values and data vectors are similar to those of the existing population of air oxidation facilities. Thus, since the national statistical profile contains 59 data vectors, each data vector and associated impacts of population control represents 1/59 of the existing population to be analyzed for control.

F.2.4 Calculation of Baseline Control Level

As mentioned earlier, the data base was constructed from uncontrolled emission sources. However, some control is currently being applied to the sources as required by current State implementation plans (SIP's) or other regulations. Furthermore, modified SIP's are projected to be in effect in ozone NAAQS nonattainment areas requesting extension. These modified SIP's would reflect the level of control recommended in the SOCMI air oxidation Control Techniques Guideline (CTG) document. In order to modify the collection of data vectors to account for projected baseline control, an analysis of the SIP requirements and an adjustment of the profile is required.

A weighted average of current control requirements appears to provide the closest approximation of current VOC control levels. The baseline analysis assumes that the statistical profile of data vectors adequately represents the population of existing air oxidation processes within each State. An annual emissions value was calculated for each data vector from its hourly emissions value. These values were summed to give a total annual emissions value for the profile. Each data vector was analyzed in order to estimate whether a plant with such offgas characteristics would be required to reduce VOC emissions by a given SIP. For each data vector determined to be subject to SIP control, the annual emission reduction under SIP was calculated. The total annual emission reduction associated with the given SIP was calculated as the sum of these individual vector values. This emission reduction value was divided by the total emissions value for the profile. The result was an estimated percent reduction of emissions for a given State or for the group of nonattainment areas. The national baseline was then calculated as a weighted average of the baselines for each State and for the nonattainment areas as a separate group. In calculating the national weighted average, each individual State baseline control value was weighted by the percent of all new source VOC emissions projected to come from the given State. These emission percentages were estimated in the following way: for each new facility projected to be built in a given State, the projected plant capacity was multiplied by the estimated average emission factor for the given process.[1,2] The resulting plant emissions estimates were summed according to State, and percentages calculated for each State to give the weighting factors. The nonattainment areas requesting extension were taken as a unit, were treated in the same manner. Analysis shows that the estimated baseline control level attributable to the SIP's is 72 percent. Consequently, a 72 percent VOC reduction from the uncontrolled level is used as the baseline level for analysis of the regulatory alternative impacts.[3]

F.3 FLOW PREDICTION

Because information on offgas flowrates was unavailable for some small-volume air oxidation chemicals, a method for estimation of offgas flowrate has been developed. Offgas flowrate is the major determinant of thermal oxidizer size and capital cost.

Operation of a thermal oxidizer is less dependent on many process and waste stream considerations than other control devices and, consequently, is the only demonstrated VOC control technology universally applicable to SOCMI air oxidation processes. Furthermore, thermal oxidation can achieve a high level of VOC control and requires only a limited amount of vent stream data (i.e., corrosion propertieis, emission rate, flow, and heat content) to determine incinerator costs and associated emission reduction.

The main factor for capital cost evaluation of a thermal oxidizer is the total offgas flowrate. Since the total offgas flowrate is not an easily obtainable parameter, a statistical estimation procedure has been developed.

As described in Chapter 3 of this document, the only determinant for classification as an air oxidation chemical is the process by which the chemical is manufactured. Despite the large variation in reaction types used to produce air oxidation chemicals, all air oxidation processes have one characteristic in common: the requirement that oxygen from the air be mixed with certain organic compounds. As a result, large quantities of inerts, mainly nitrogen and unreacted oxygen, must be vented from the process. This stream flowrate determines the thermal oxidizer size and cost. Thus, the amount of air introduced into the reaction system determines to a large extent the capital cost of thermal oxidation. There are several reaction characteristics that determine the amount of offgas vented to the atmopshere, including:

1. Reaction stoichiometry,
2. Reaction phase, and
3. Explosion hazard.

A theoretical discussion of the contribution of each of these factors to the excess air requirements is contained in Chapter 3.

The effect of reaction stoichiometry on offgas flowrate can be calculated for each air oxidation process based on available data regarding the overall, balanced production reaction. If an accurate overall reaction is developed which includes all significant side reactions, a "stoichiometric flowrate" can be calculated. This stoichiometric flowrate is the flowrate necessary to provide the exact amount of oxygen required to give the annual production. Therefore, a ratio of actual flowrate to stoichiometric flowrate (flow ratio) can be defined as a measure of the amount of excess air used.

In order to quantify the effects of reaction phase and explosion hazard on the flow ratio, multiple linear regression techniques were employed.

Because explosion hazards are very different for liquid-phase reactions than for vapor-phase reactions, the statistical profile was divided in two according to reaction phase. Actual values of the flow ratio were calculated for each data vector. For liquid-phase data vectors, multiple linear regression showed no correlation between flow ratio and parameters related to explosion hazard. However a clearly defined ceiling value of three was observed for the actual flow ratios.

TABLE F-7. A COMPARISON OF THE EIGHT CONSIDERED FORMS OF THE F PREDICTOR EQUATION

Parameter	Equation Number							
	1	2	3	4	5	6	7	8
Intercept	-10.1	-8.94	-4.69	-0.935	-	-	-	-
EL	-	-	-	-	-	-	-	1.13
TR/(TI·EL)	15.8	15.3	16.0	7.58	6.26	7.99	9.49	17.2
LN(TR/(TI·EL))	-5.11	-4.66	-5.29	-	-	-	-	-
Heat	-	-	-	-	-	-	-	-
1/EL	-	-	-	-	-	-	-0.002	-7.04
LN(KTR/KTI)	-	-	9.38	-	-	-	-	-
TR	0.001	-	-	-	-	-	-	-
TR/TI	-	-	-4.75	-	-	-1.04	-1.26	-4.98
Coefficient of Determination (R^2)	0.950	0.942	0.976	0.833	0.894	0.924	0.952	0.989
F-Statistic Value for the Model	254	370	391	210	364	255	269	896
Significance Probability of Least Significant Parameter	0.1594	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
Degrees of Freedom	40	41	39	42	43	42	41	40
Parameters	3	2	4	1	1	2	3	4
Observations	44	44	44	44	44	44	44	44

Key:

EL = Lower explosive limit.
TR = Reaction temperature (^oC).
KTR = Reaction temperature (^oK).
TI = Autoignition temperature (^oC).
KTI = Autoignition temperature (^oK).
Heat = Absolute value of global heat of reaction (CAL/g-mole).

The composite parameters considered in the vapor-phase regression analysis were all functions of four explosion hazard-related offgas parameters. These were reaction temperature, global heat of reaction, explosive limit of the most expensive component, and autoignition temperature of the most explosive component. Ten composite parameters were constructed. Eight model equations were developed, each of which contained from one to five of the composite parameters. A comparison of the linear regression results for these eight equations is given in Table F-7.

Equation 8 was chosen as the best flow ratio predictor on the basis of its high model F-statistic value and coefficient of determination (R^2 value). Each of the four parameters in the chosen equation were significant at the 0.0001 level. The chosen equation is:

$$\text{FLOW RATIO} = -4.98\ (TR/TI) - 7.04\ (1/EL) + 17.2\ (TR/TI) \cdot (1/EL) + 1.13\ (EL),$$

where:

TR = reaction temperature (^{o}C).

TI = autoignition temperature (^{o}C).

EL = explosive limit (volume percent).

Some summary statistics of the chosen equation are given in Table F-8. A comparison of actual and predicted flow ratios is given in Table F-9.

TABLE F-8. SUMMARY STATISTICS OF THE CHOSEN F PREDICTOR EQUATION

Parameter	Estimate	Standard Error of Estimate	Significance Probability
TR/TI	-4.98	0.31	0.0001
1/EL	-7.04	0.47	0.0001
(TR/TI)·(1/EL)	17.2	0.63	0.0001
EL	1.13	0.09	0.0001

Model F Value = 896

Coefficient of Determination (R^2) = 0.989

Coefficient of Variation = 15.8

Significance Probability of Model = 0.0001

Key:

EL = Lower explosive limit.

TR = Reaction temperature (°C).

TI = Autoignition temperature (°C).

TABLE F-9. EFFECTIVENESS OF THE F_3 PREDICTOR

OBS	Actual	Predicted	Relative Error	Upper 90% Confidence Limit
1	1.65	1.29	0.27	2.02
2	0.75	1.29	0.42	2.02
3	1.55	1.29	0.20	2.02
4	1.92	1.29	0.49	2.02
5	1.19	1.24	0.04	1.98
6	2.81	3.28	0.15	4.07
7	12.7	12.4	0.02	13.2
8	12.0	12.4	0.04	13.2
9	12.7	12.4	0.02	13.2
10	3.38	3.28	0.03	4.07
11	1.30	1.28	0.01	2.00
12	0.98	1.28	0.24	2.00
13	1.83	1.28	0.43	2.00
14	2.04	1.28	0.60	2.00
15	1.58	1.28	0.24	2.00
16	0.98	1.28	0.24	2.00
17	0.91	1.28	0.29	2.00
18	0.95	1.28	0.25	2.00
19	1.19	1.28	0.07	2.00
20	1.99	2.16	0.08	2.87
21	2.26	2.16	0.05	2.87
22	2.51	2.16	0.16	2.87
23	2.74	2.16	0.27	2.87
24	2.40	3.05	0.21	3.78
25	2.96	3.05	0.03	3.78
26	3.56	3.05	0.17	3.78
27	2.88	3.05	0.06	3.78
28	3.31	3.05	0.09	3.78
29	2.99	3.05	0.02	3.78
30	2.96	3.05	0.03	3.78
31	2.77	1.64	0.53	2.37
32	2.28	1.64	0.40	2.37
33	2.00	1.64	0.22	2.37
34	1.30	1.64	0.20	2.37
35	1.57	1.64	0.04	2.37
36	1.55	1.64	0.05	2.37
37	2.09	1.64	0.27	2.37
38	2.29	1.64	0.40	2.37
39	1.93	2.16	0.11	2.90
40	1.87	2.16	0.13	2.90
41	1.87	2.16	0.13	2.90
42	1.58	2.16	0.27	2.90
43	1.91	1.60	0.33	2.42
		MEAN:	0.19	
		MEDIAN:	0.16	

F.4 REFERENCES FOR APPENDIX F

1. Darby, W.P. et. al., Regulation of Air Oxidation Processes Within the Synthetic Organic Chemical Manufacturing Industry: Background Information and Analysis. St. Louis, Washington University, 1981. Appendix A.

2. Control of Volatile Organic Compound Emissions from Air Oxidation Processes in Synthetic Organic Chemical Manufacturing Industry. Draft Control Techniques Guideline Document. July 1981. Appendix D.

3. Memo from Galloway, J., EEA, to SOCMI Air Oxidation File. July 29, 1981.

APPENDIX G: COST ANALYSIS SPECIAL TOPICS

APPENDIX G: COST ANALYSIS SPECIAL TOPICS

G.1 INTRODUCTION[1,2]

The purchase cost estimates for individual pieces of control equipment are discussed in this appendix in relation to the raw vendor data on which the estimates are based. Independent vendor estimates are also compared with the purchase costs. The method of estimating installed costs from component installation factors is discussed. Graphs of the installed costs for several types of control equipment, as a function of flowrate, are presented. Graphs are also presented for total installed capital costs for the control systems, and the derivations of capital cost equations from these graphs are discussed. Details of the chemical process-specific costing methodology are given.

G.2 CONTROL EQUIPMENT PURCHASE COSTS

G.2.1 Thermal Oxidizer

EEA obtained data from the three vendors which provided combustion chamber cost data to Enviroscience. The three sets of vendor quotations agreed with each other well. The Enviroscience purchase cost curve represents a conservative "envelope" that is higher than the vendor data for all equipment sizes.

Vendor A quoted costs for four equipment sizes for each of six different incineration temperatures. Vendor B quoted costs for 14 equipment sizes for each of four different temperatures. Vendor C quoted costs for six equipment sizes for each of two different temperatures. These data constitute an abundance of observations for derivation of reasonably accurate equations for the relation of capital cost to offgas flowrate.

EEA independently obtained data from two additional vendors. Each of these quoted costs for two equipment sizes at one temperature. Their quotations essentially agreed with those of the vendors contacted by Enviroscience.

G.2.2 Recuperative Heat Exchanger

EEA obtained data from the two vendors which provided heat exchanger costs to Enviroscience. The two sets of vendor quotations agreed with each other well. The Enviroscience purchase cost curve represents an average that is roughly equivalent to the vendor curves.

Vendor A quoted costs for four offgas flowrates for each of two levels of heat recovery. Vendor C quoted costs for three offgas flowrates for each of two levels of heat recovery. Because heat exchanger costs were quoted as functions of heat exchange surface area, these data actually represent eight and six different equipment sizes, respectively. These data constitute an adequate number of observations for derivation of reasonably accurate equations for the relation of capital cost to offgas flowrate.

EEA independently obtained data from two additional vendors. One quoted costs for two offgas flowrates. The other quoted costs for two offgas flowrates for each of two temperatures. Their quotations essentially agreed with those of the vendors contacted by Enviroscience.

G.2.3 Waste Heat Boiler

EEA obtained data from one vendor which provided waste heat boiler costs to Enviroscience. The Enviroscience purchase cost curve represents this data well.

The vendor quoted costs for 10 offgas flowrates for each of three different temperatures. These data actually represent 30 different equipment sizes, and therefore constitute an abundance of observations for derivation of reasonably accurate equations for the relation of capital cost to offgas flowrate.

G.2.4 Fans

One vendor quoted costs for 13 sizes of fans. These data constitute an abundant number of observations for derivation of reasonably accurate capital cost equations.

G.2.5 Stack

One vendor quoted costs for four sizes of stacks. While these data constitute a minimal number of observations for accurate interpolation between given stack sizes, the relatively low cost of stacks compared to the rest of the control system makes extra accuracy unnecessary.

G.2.6 Ducts

Enviroscience used EPA 450/5-80-002 (The "GARD" Manual) as its source for duct costs.

G.3 INSTALLATION FACTORS

The Enviroscience method of estimating installed costs of combustion chamber, recuperative heat exchanger, and waste heat boiler from the original vendor cost quotations is discussed below and summarized in Table G-1. The component purchase costs represent interpolations of vendor quotations and are graphed as continuous functions of offgas flowrate. A factor of 20 percent for "unspecified equipment" was added to the budget prices of the combustion chamber and waste heat boiler. This factor was omitted for the heat exchanger. Factors were then added for 10 aspects of installation, such as insulation and piping. These factors were expressed as percentages of the budget price of the equipment in question. The overall sum of these factors plus the factor of one for the original equipment and, in two cases, the factor of 0.2 for unspecified equipment was multiplied by a factor of 1.35, which represented the impact of contingencies, fees, site development, and vendor assistance. Because the original costs seemed low, several cases were vigorously recosted. It was decided by Enviroscience that the overall installation factor would be multiplied by 1.33 to achieve a better estimate. However, Enviroscience assumed that this factor of 1.33 was due entirely to underestimates of the factors for the 10 aspects of installation. An alternative correction factor was therefore calculated which, when multiplied by the sum of the 10 installation component factors, would result in the values of the same overall installation factor as given by the 1.33 estimate. The values of this correction factor were 1.7 for the combustion chamber, 2.1 for the heat exchanger, and 1.9 for the boiler. The values of the final overall new source installation factor were 4.0, 2.5, and 3.5 for the combustion chamber, heat exchanger, and waste heat boiler, respectively.

In order to estimate total installed capital costs in the case of modified or reconstructed facilities, retrofit installation factors were then developed from the new source factors. Because cramped plant conditions will make a longer time of installation necessary, the installation labor cost will increase. For each of the nine aspects of installation other than engineering, freight, and taxes, it is assumed that 50 percent of the component installation factor represents labor costs. These labor costs were assumed to double in each case. Therefore, each of the nine component

TABLE G-1. INSTALLATION COMPONENT FACTORS (% OF BUDGET PRICE OF MAIN EQUIPMENT)

Installation Component	Combustion Chamber			Recuperative Heat Exchange			Waste Heat Boiler		
	New Source	Retrofit Labor	Retrofit Special Expenses	New Source	Retrofit Labor	Retrofit Special Expenses	New Source	Retrofit Labor	Retrofit Special Expenses
Foundation	6	9	9	6	9	9	8	12	12
Insulation	6	9	9	2	3	3	2	3	3
Structures	2	3	10	1	2	10	-	-	-
Erection	15	22	45	10	15	30	20	30	60
Piping	20	30	60	-	-	-	10	15	30
Painting	5	8	8	2	3	6	-	-	-
Instruments	15	22	22	-	-	-	4	6	6
Electrical	5	8	15	-	-	-	-	-	-
Fire Protection	1	2	2	-	-	-	1	2	2
Engineering, Freight and Taxes	29	29	29	21	21	21	29	29	29
TOTAL Factors	104	142	209	42	53	79	74	97	142

	Combustion Chamber	Heat Exchanger	Waste Heat Boiler
Budget Price	1	1	1
Unspecified Equipment	0.2	0	0.2
Total installation Component: New Source	1.04	0.42	0.74
Retrofit	2.09	0.79	1.42
Contingencies, Fees, Site Development	1.35	1.35	1.35
Overall Correction Factor	1.33	1.33	1.33
Total Installation Component Correction Factor	1.7	2.1	1.9
Overall Installation Factor: New Source	4.0	2.5	3.5
Retrofit	6.5	3.5	5.3

Formulas: (1) Overall New Source Installation Factor = (Budget Price Factor + Unspecified Equipment Factor + Total New Source Installation Component Factor) x Contingencies Factor x Overall Correction Factor
Example (Combustion Chamber): 4.0 = (1 + 0.2 + 1.04) x 1.35 x 1.33

(2) Total Installation Component Correction Factor = ((Overall New Source Installation Factor ÷ Contingencies Factor) - Budget Price Factor - Unspecified Equipment Factor) ÷ Total New Source Installation Component Factor
Example (Combustion Chamber): 1.7 = ((4.0 ÷ 1.35) - 1 - 0.2) ÷ 1.04

(3) Overall Retrofit Installation Factor = (Budget Price Factor + Unspecified Equipment Factor + (Total Retrofit Installation Component Factor x Total Installation Component Correction Factor)) x Contingencies Factor
Example (Combustion Chamber): 6.5 = (1 + 0.2 + (2.09 x 1.7)) x 1.35

factors was assumed to increase by 50 percent due to labor. Added expense was expected for four of the factors: structures, piping, erection, and electrical. Such expense might be due to a steel or concrete deck for the equipment, extra circuit breakers, and about 500 feet of extra ducting. The factors for erection, piping, and electrical, after inclusion of the labor increase, were doubled. The factor for structures for the combustion chamber and heat exchanger was assumed to increase to 10 percent. The overall retrofit installation factors, calculated as above, for the combustion chamber, heat exchanger, and boiler were 6.5, 3.5, and 5.3, respectively.

In order that the Enviroscience total installed cost curves could be used directly, one overall retrofit-to-new source correction factor was developed. The individual correction factors for the combustion chamber, heat exchanger, and boiler were 1.625, 1.4, and 1.514, respectively. In order to give a conservative estimate of total installed costs, the value of 1.625 was used for the retrofit-to-new source correction factor.

G.4 INDIVIDUAL COMPONENT INSTALLED COSTS

Installed capital costs for a thermal oxidizer designed for a 870°C (1600°F) combustion temperature and 0.75 second residence time are given in Figure G-1. Recuperative heat exchanger installed capital costs are given in Figure G-2. Installed capital costs for inlet ducts, fans, and stack, for systems with and without heat recovery, are given in Figure G-3 and G-4, respectively. The above equipment units constitute the components of a control system for nonchlorinated vent streams.

Figures G-5 and G-6 give the installed capital costs for a thermal oxidizer at 1200°C (2200°F) and 0.75 second residence time and for a waste heat boiler, respectively. The installed capital costs of a scrubber including quench chamber are given in Figure G-7. Figure G-8 gives installed capital costs for ducts, fans, and stack for a system employing a waste heat boiler.

G.5 TOTAL CONTROL SYSTEM INSTALLED CAPITAL COSTS

Total installed capital costs of a thermal oxidation system for control of nonchlorinated vent streams are given in Figure G-9. The design conditions are 870°C (1600°F) and a 0.75 second residence time. Figure G-10 gives the total installed capital costs of a thermal oxidation system for control of chlorinated vent streams at 1200°C (2200°F). These conditions were

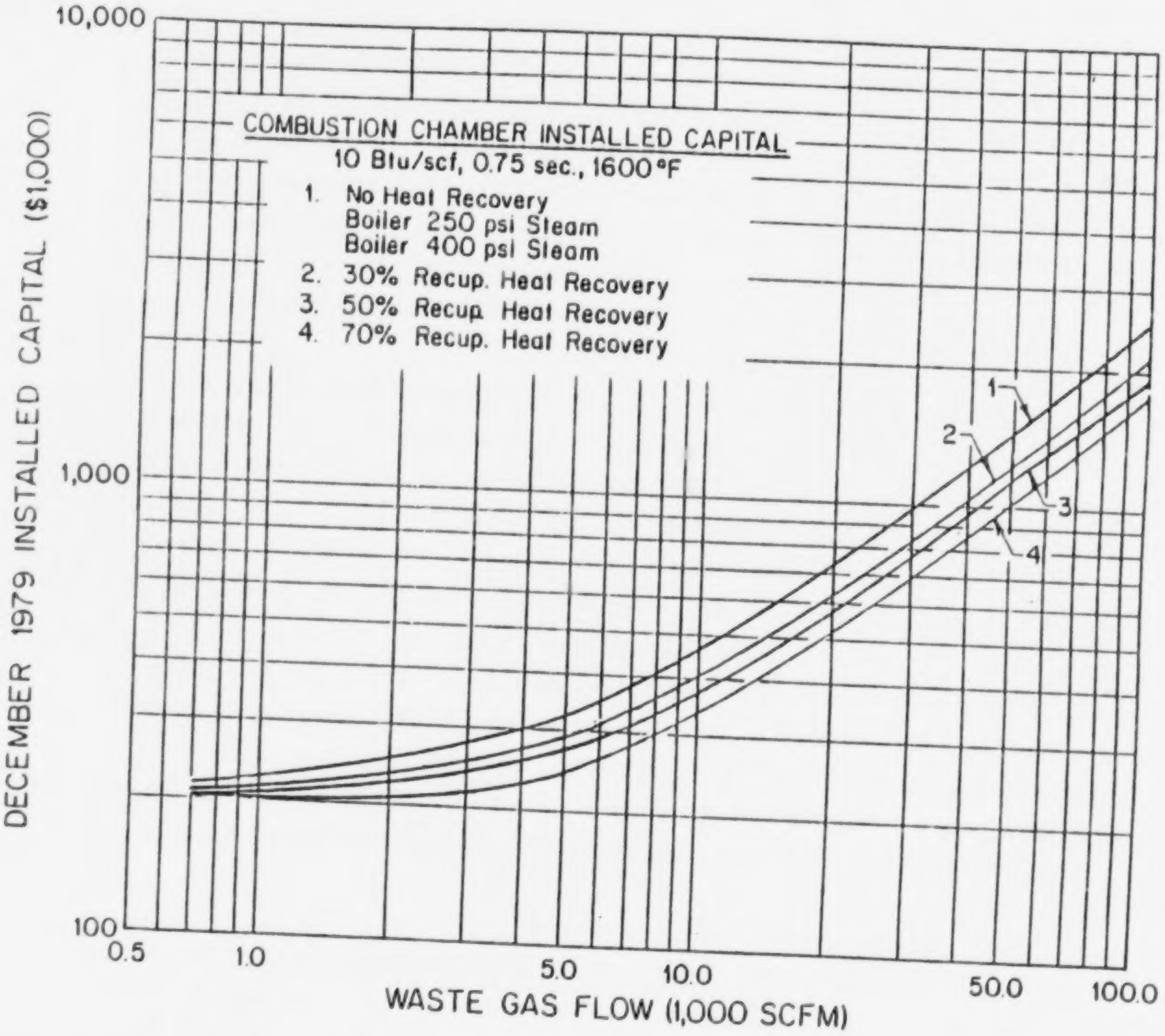

Figure G-1. Installed capital cost for the combustion chamber with waste gas heat content = 10 Btu/scf, residence time = 0.75 sec, and combustion temperature = 1600°F.

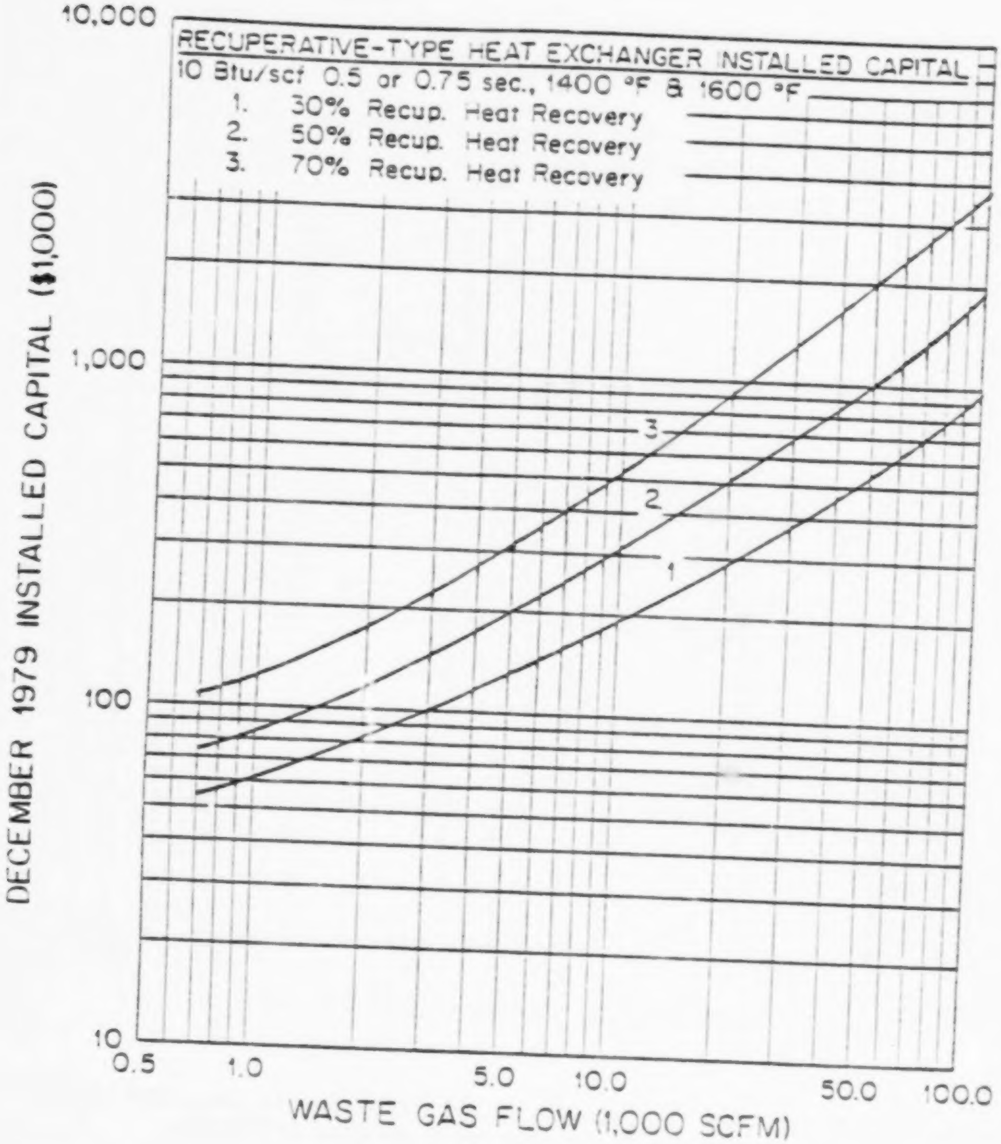

Figure G-2. Installed capital cost for recuperative-type heat exchangers with the waste gas heat content = 10 Btu/scf.

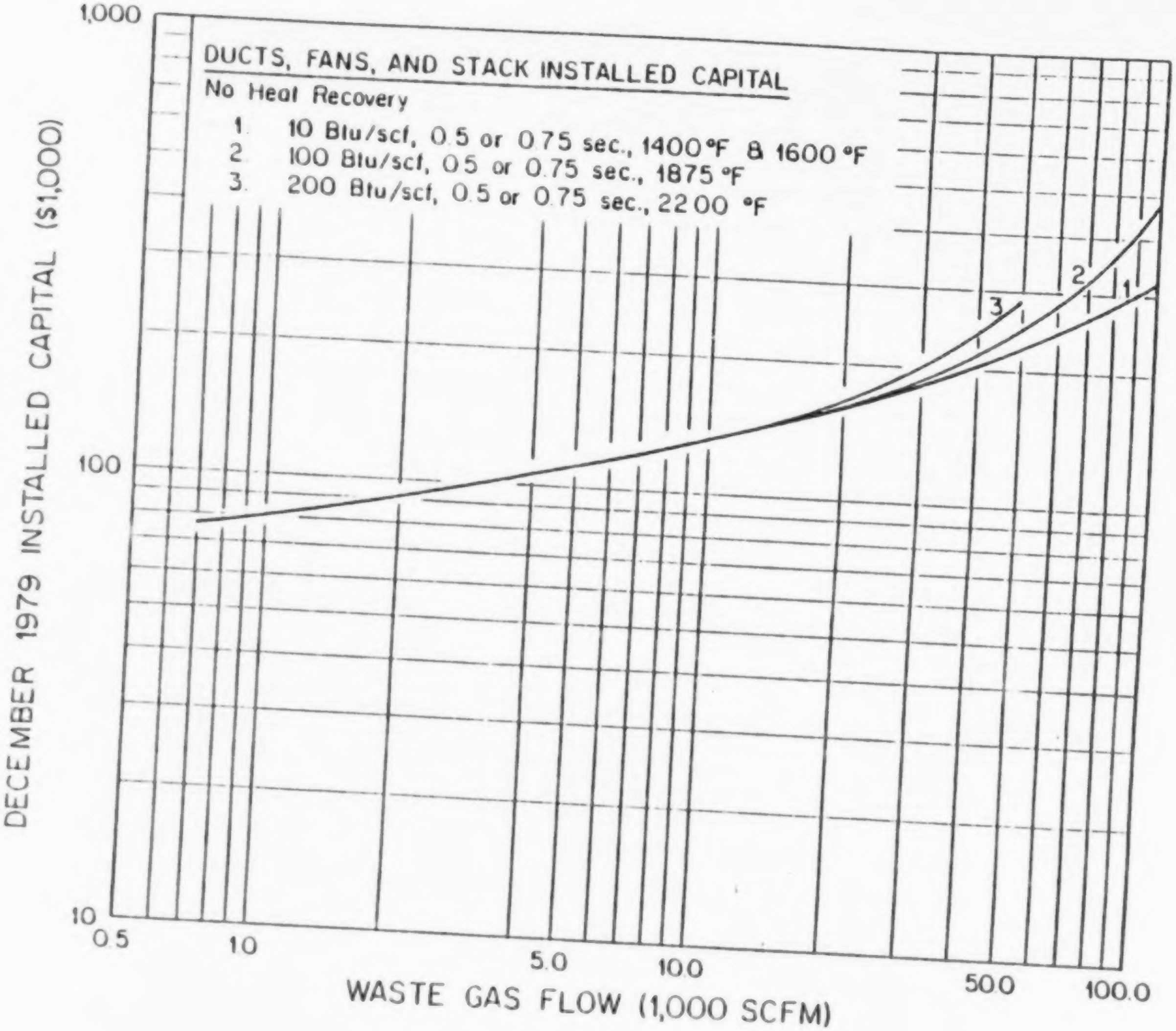

Figure G-3. Installed capital costs for inlet ducts, waste gas, and combustion air fans and stack for system with no heat recovery.

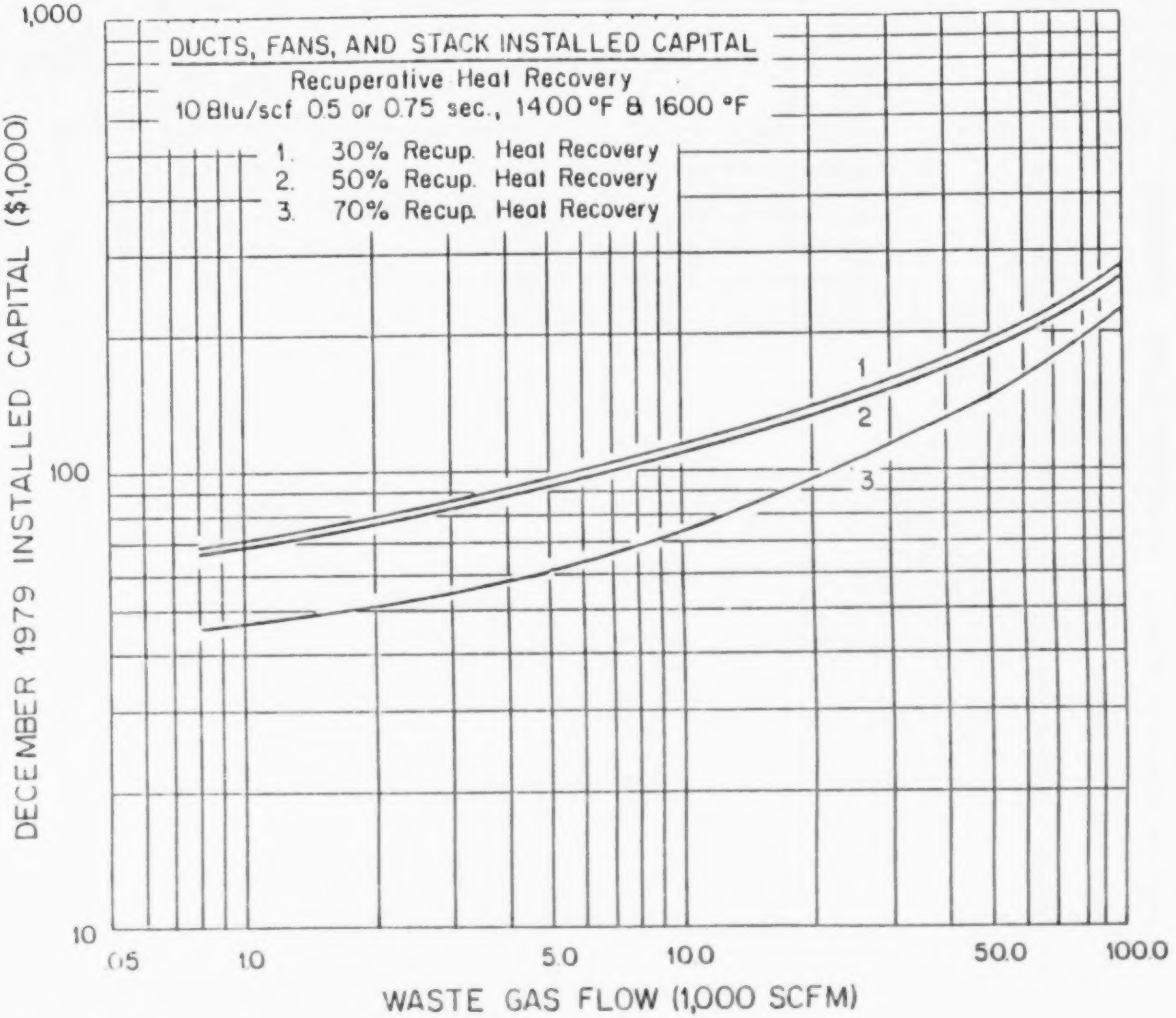

Figure G-4. Installed capital costs for inlet ducts, waste gas, and combustion air fans and stack for system with no heat recovery.

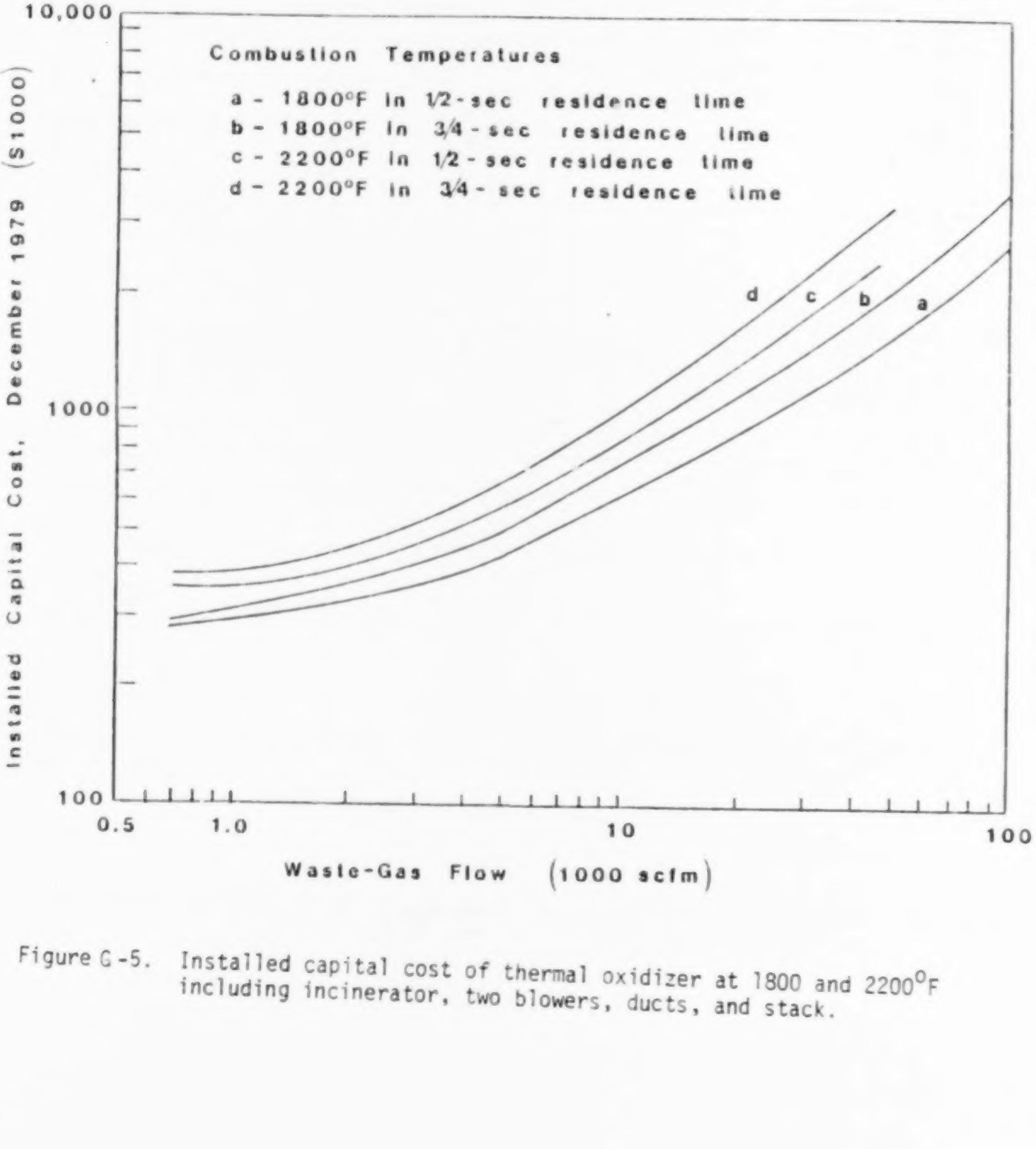

Figure G-5. Installed capital cost of thermal oxidizer at 1800 and 2200°F including incinerator, two blowers, ducts, and stack.

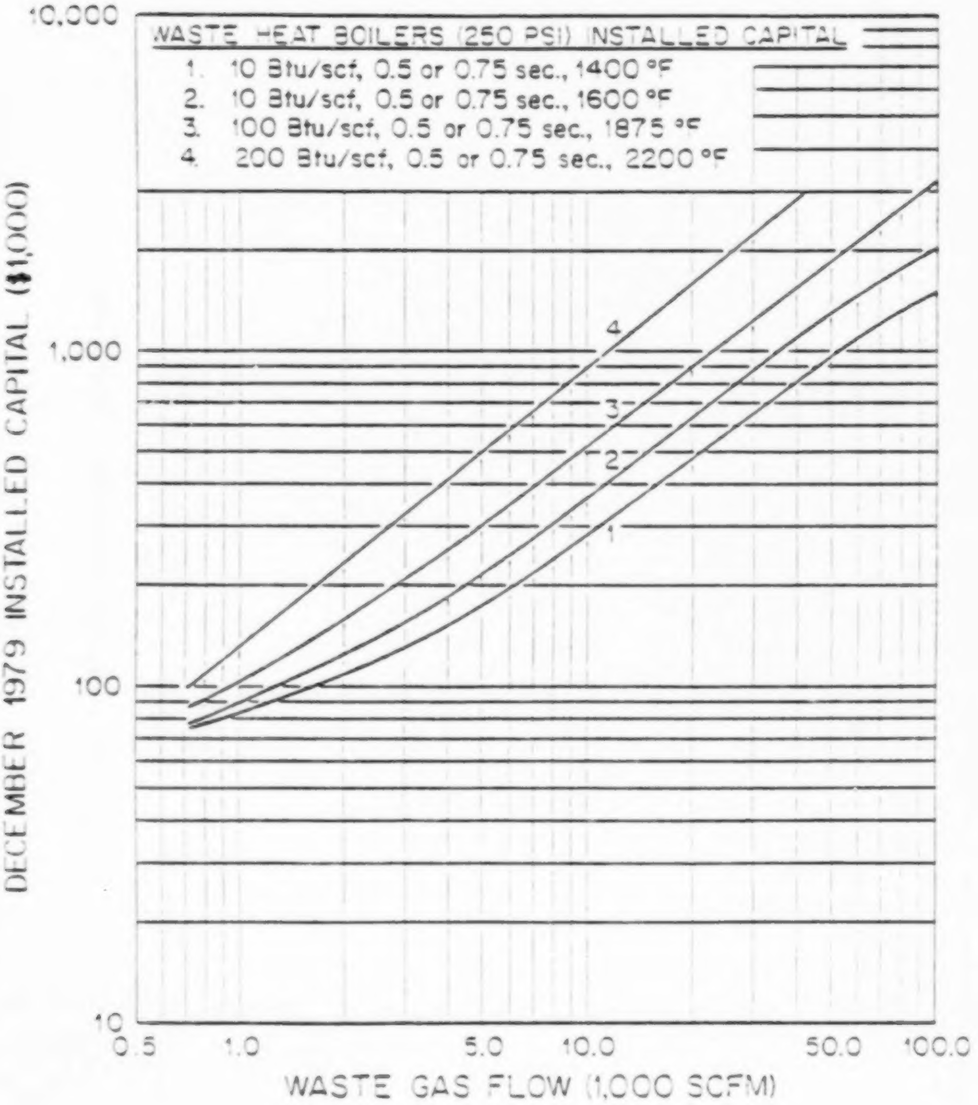

Figure G-6. Installed capital cost for waste heat boiles (250 psi).

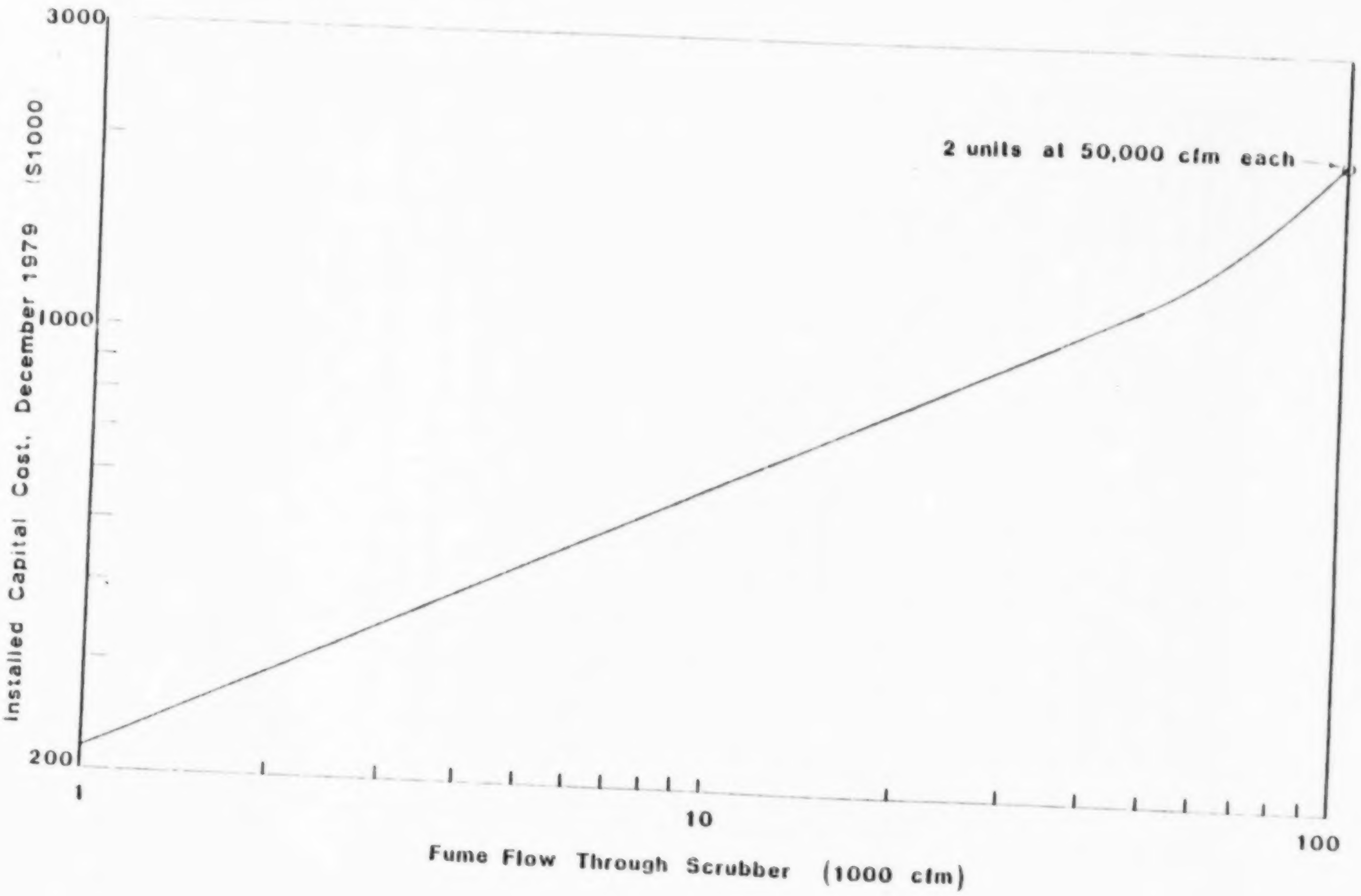

Figure G-7. Installed capital cost of the scrubber including quench chamber.

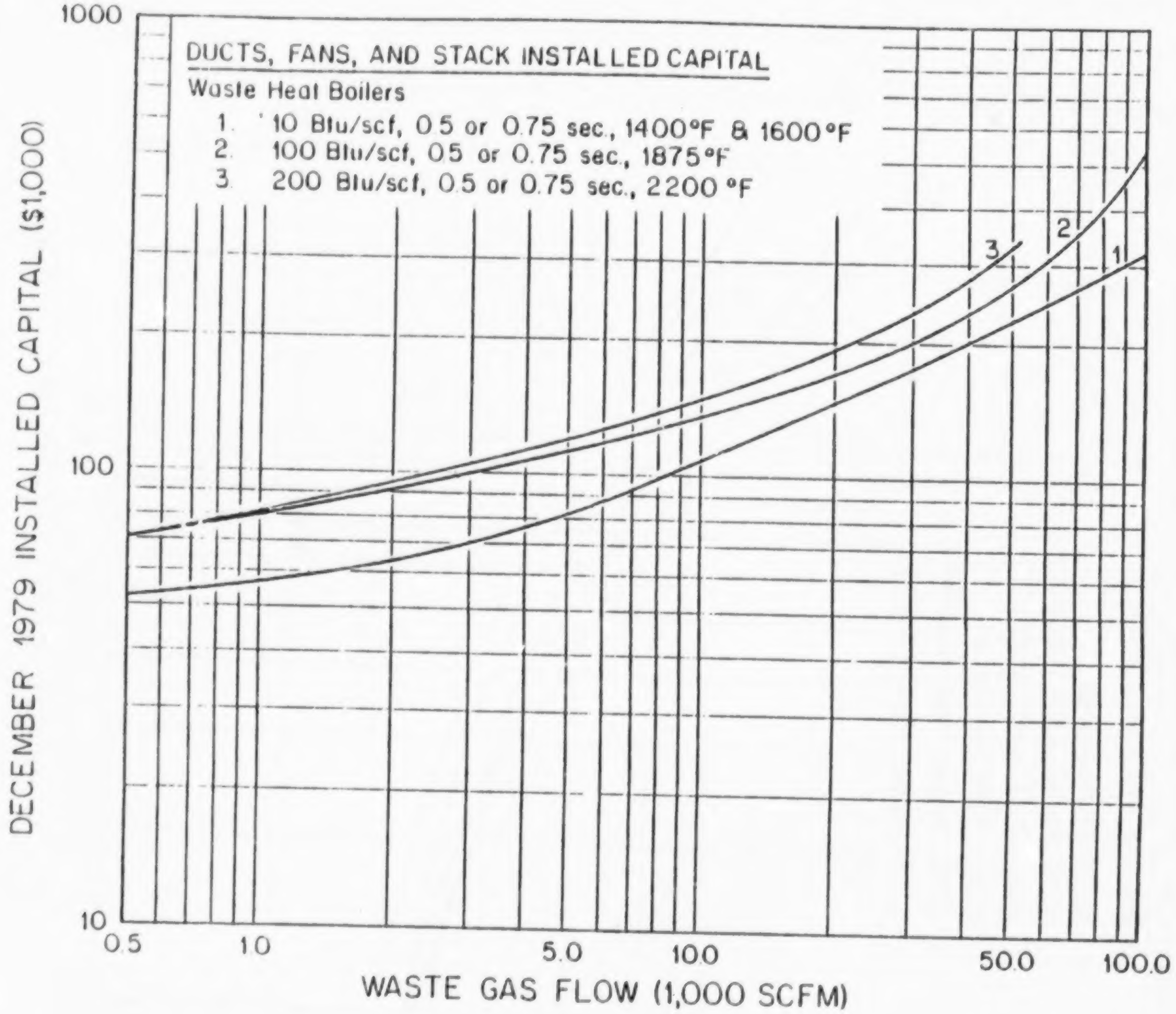

Figure G-8. Installed capital for inlet ducts, waste gas, and combustion air fans and stack with waste heat boilers.

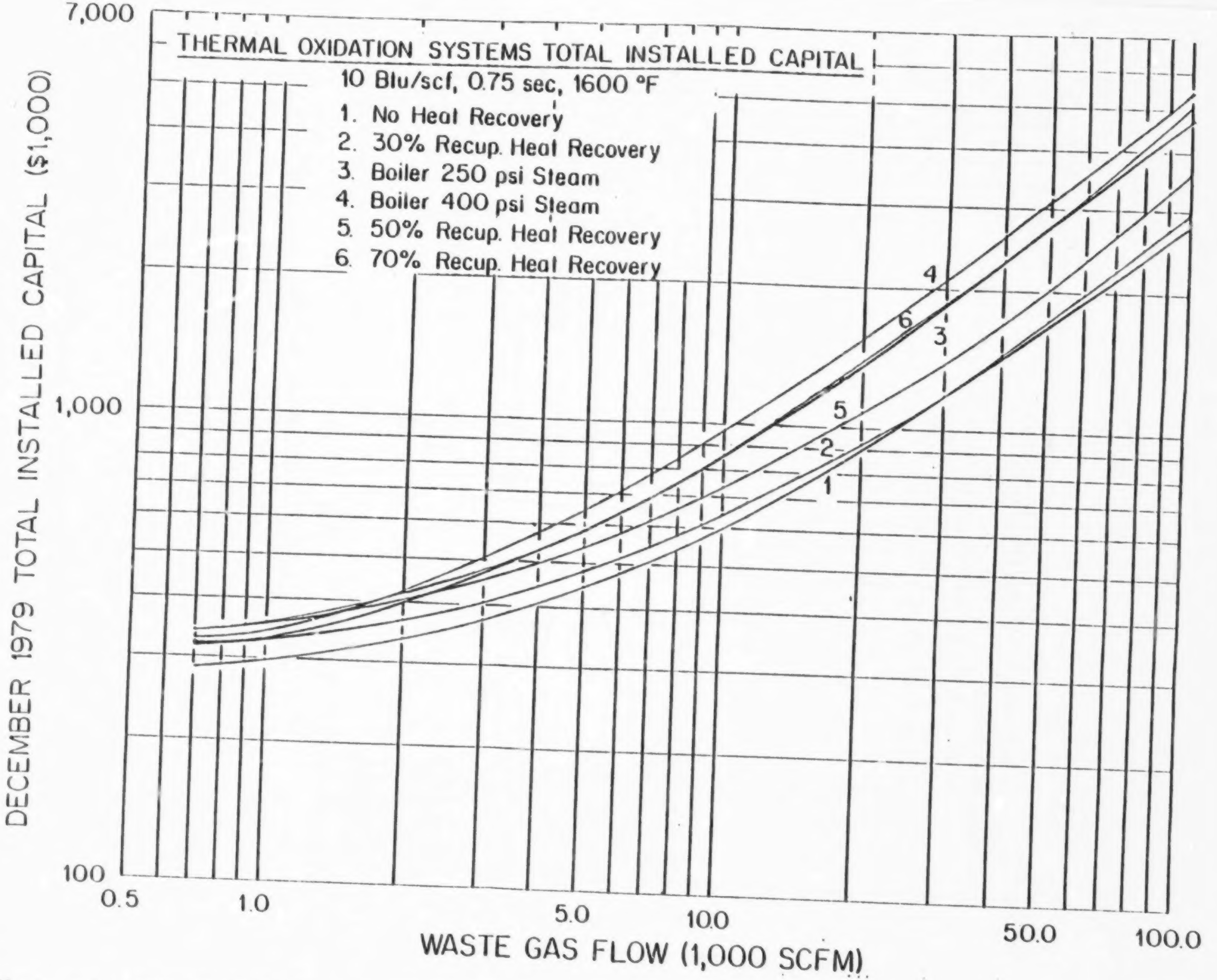

Figure G-9. Total installed capital cost for thermal oxidation systems with waste gas heat content = 10 Btu/scf, residence time = 0.75 sec, and combustion temperature = 1600°F.

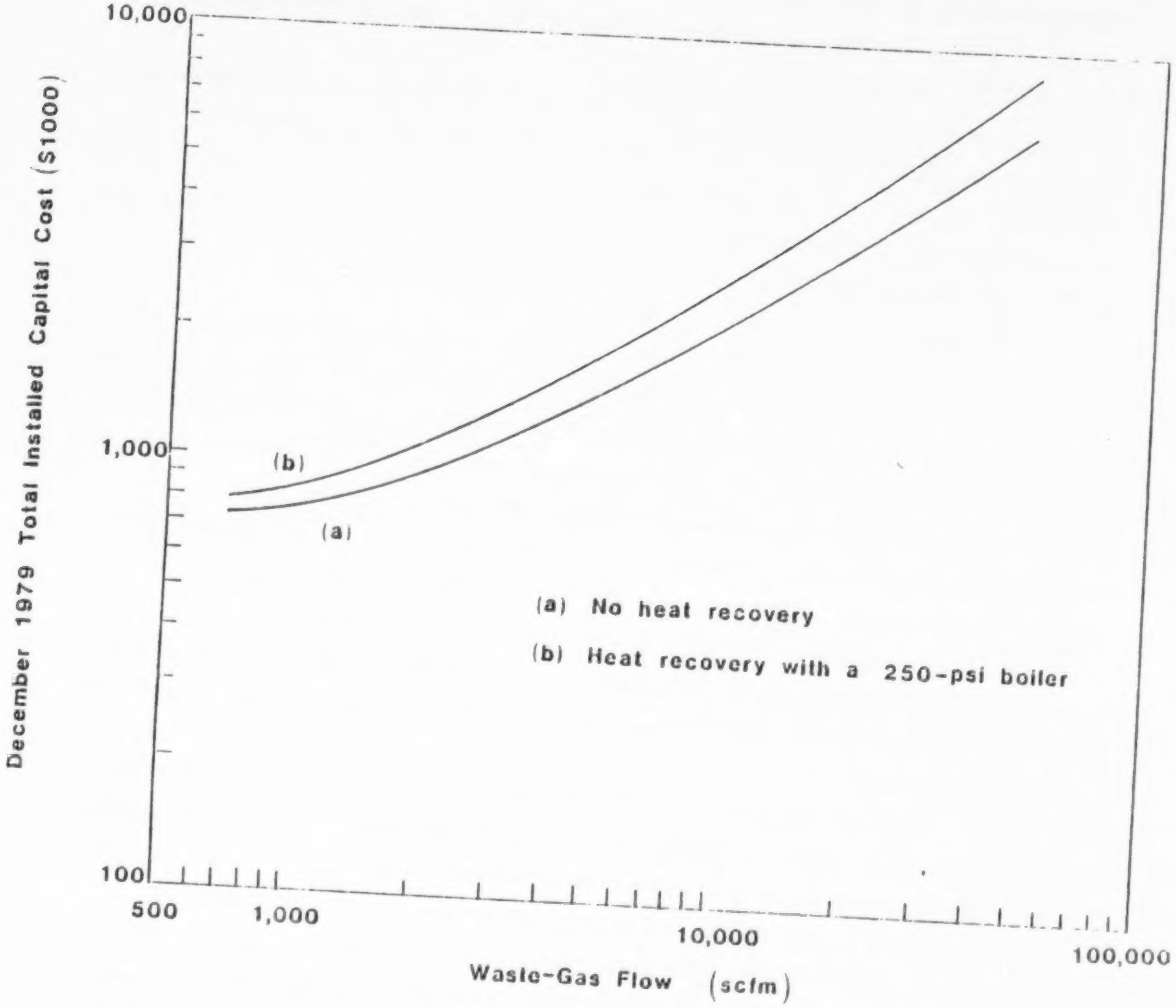

Figure G-10. Total installed capital cost for thermal oxidation systems with a scrubber at a residence time of 0.5 sec, a combustion temperature at 2200°F, and a waste gas heat content of 1 Btu/scf.

corrected to 1090°C (2000°F) and a one second residence time. The combustion chamber volume correction factor of 1.14 represents the product of a temperature correction, combustion air flowrate correction, and residence time correction. The development of the total installed capital cost equations for each design from the Enviroscience cost curves is discussed in Reference 3.

G.6 CHEMICAL PROCESS-SPECIFIC COSTS

As discussed in Chapter 8, costs for each specific chemical manufacturing process were developed for use in the economic analysis presented in Chapter 9. Capital, annualized, operating, and control costs (cents per kg of product) were projected for each chemical process. This section presents details of the costing methodology and the process-specific parameters, which are given in Table G-2.

Several of these processes, as discussed in Chapter 8, produce by-products and/or co-products. A single value of capital cost, annualized cost, and operating cost was projected for such processes. In calculating the control costs (cents per kg of product) for by-products and co-products, the total annualized cost for the process was attributed to each by-product/co-product. Likewise, the total production of all by-products and co-products was used in calculating the control cost of each by-product/co-product. Therefore, the control costs of the by-product(s)/co-product(s) are equal. This method of projecting contol costs is equivalent to sharing the total annualized cost of the process by weight of product.

The method of calculating chemical process-specific costs differed from the methods used in Chapter 8 in several respects. For those processes employing a vapor-phase air oxidation reaction (discussed in Chapter 3), offgas flowrates were predicted according to the method discussed in Appendix F. An after-tax discount rate of 8.5 percent was used. The actual offgas oxygen concentrations were considered in estimating offgas flowrates and capital costs. Chemical processes with offgas net heating values that fall in Categories D and E were assumed to have a heat recovery credit due to use of a waste heat boiler. No diluttion of offgas was assumed for processes with heating values within the Category E range. For processes with heating values within the range of Category C, offgas dilution sufficient to permit use of 70 percent recuperative heat recovery

TABLE G-2. CHARACTERISTICS OF SPECIFIC CHEMICAL PROCESSES

Chemical (Process)[a]	Plant Capacity (Thousand Mg/yr)	Molar Oxygen to Product Ratio	Product Molecular Weight	F[b]	Capacity Utilization Factor	Net Heating Value (MJ/scm)
Acetaldehyde	159	0.500	44.50	3.000	0.740	.009
Acetic Acid (Wacker)	79	0.500	60.05	3.000	0.887	.233
Acetic Acid (Butane)	311	1.220	58.54	1.472	0.732	.009
Formic Acid	311	1.220	58.54	1.472	0.732	.009
Methyl Ethyl Ketone	311	1.220	58.54	1.472	0.732	.009
Propionic Acid	311	1.220	58.54	1.472	0.732	.009
Acetone (Cumene)	40	0.500	78.74	1.736	0.777	.065
Acetophenone	40	0.500	78.74	1.736	0.777	.065
Cumene Hydroperoxide	40	0.500	78.74	1.736	0.777	.065
Methyl Styrene	40	0.500	78.74	1.736	0.777	.065
Phenol	40	0.500	78.74	1.736	0.777	.065
Acrylic Acid	91	1.322	66.38	2.569	0.770	1.53
Acrolein	91	1.322	66.38	2.569	0.770	1.53
Acrylonitrile (Propene)	120	1.375	46.60	1.917	0.866	.447
Acetonitrile	120	1.375	46.60	1.917	0.866	.447
Hydrogen Cyanide	120	1.375	46.60	1.917	0.866	.447
Anthraquinone	1.8	1.500	208.20	26.600	0.770	.009
Benzaldehyde	1.4	1.000	106.10	3.000	0.685	.037
Benzoic Acid	4	1.500	122.10	3.000	0.685	.037
1,3-Butadiene	27	0.750	54.09	10.000	0.793	.345
p-t-Butyl Benzoic Acid	2.7	1.500	178.23	3.000	0.770	.297
n-Butyric Acid	6.4	1.000	88.10	3.000	0.770	.074

TABLE G-2 (Continued). CHARACTERISTICS OF SPECIFIC CHEMICAL PROCESSES

Chemical (Process)[a]	Plant Capacity (Thousand Mg/yr)	Molar Oxygen to Product Ratio	Product Molecular Weight	F[b]	Capacity Utilization Factor	Net Heating Value (MJ/scm)
Crotonic Acid	5.9	0.500	86.09	3.000	0.770	.009
Cyclohexanol	45	0.750	99.15	3.000	0.874	.429
Cyclohexanone	45	0.750	99.15	3.000	0.874	.429
Dimethyl Terephthalate	227	3.000	194.18	1.762	0.792	.084
Terephthalic Acid	227	3.000	194.18	1.762	0.792	.084
Ethylene Oxide	45	1.500	44.05	1.183	0.839	.363
Formaldehyde (Metal Oxide)	6.8	0.500	30.03	1.638	0.686	.103
Formaldehyde (Silver)	8.6	0.330	30.03	1.635	0.686	2.82
Glyoxal	1.4	2.070	58.04	1.708	0.770	.009
Hydrogen Cyanide	1.4	2.320	27.03	1.183	0.496	3.29
Isobutyric Acid	4.5	0.500	88.10	3.000	0.770	.960
Isophthalic Acid	109	3.000	166.13	3.000	0.543	.093
Maleic Anhydride (Benzene)	12	8.540	98.06	1.646	0.689	.317
Maleic Anhydride (Butane)	27	9.000	98.06	1.761	0.689	.447
Phthalic Anhydride (Xylene)	16	3.000	148.10	6.652	0.756	.308
Phthalic Anhydride (Naphthalene)	39	5.170	143.10	1.774	0.756	.140
Propionic Acid (Propionaldehyde)	86	0.500	74.08	1.100	0.410	1.26
Propylene Oxide (Ethylbenzene)	635	0.520	83.30	3.000	0.832	.028
Styrene	635	0.520	83.30	3.000	0.832	.028
Ethylene Dichloride	59	0.500	98.96	1.156	0.731	.680

[a] Chemicals that are co-products or by-products of a particular air oxidation process are indented.

[b] F is the predicted ratio of actual flowrate to stoichiometric flowrate.

was assumed, if such dilution would result in lower projected annualized costs. Such processes were assumed to employ an offgas dilution sufficient to yield a net heating value of 0.48 MJ/scm and place the process within design Category B. Such a dilution was assumed for acrylonitrile (propylene ammoxidation process) and its by-products.

The ratios of actual flowrate to stoichiometric flowrate (F values) for vapor-phase processes were calculated according to the following equation, which was statistically developed in Appendix F:

$$F = -4.98\,(TR/TI) - 7.04\,(1/EL) + 17.2\,(TR/TI) \cdot (1/EL) + 1.13\,(EL)$$

Where:

TR = reaction temperature (^{o}C).

TI = autoignition temperature (^{o}C) of most explosive organic compound present.

EL = lower explosive limit (volume percent) of most explosive organic compound present.

For liquid-phase processes, an F value of three was assumed, except for acetic acid (butane oxidation) and dimethyl terephthalate/terephthalic acid, where the actual F values were known to be lower.[4]

Flowrates were predicted from the F values and process parameters according to the following equation:

$$\text{Flow} = 203.5 \cdot \text{Capacity} \cdot \text{MOR} \cdot F \div \text{MW}$$

Where:

Flow = offgas flowrate (scm/min).

Capacity = plant capacity (thousand Mg/yr)

MOR = molar oxygen to product ratio for the global air oxidation reaction.

F = ratio of actual flowrate to stoichiometric flowrate.

MW = product molecular weight.

The 203.5 conversion factor has the units (scm/g-mole) (yr/MM min). For those processes with by-products, the plant capacity is a total capacity for all products The molar oxygen ratios for such processes represent moles of oxygen per total moles of all products, according to the balanced global reaction. The product molecular weight given in Table G-2 for such processes is an average of by-product/co-product molecular weights. This average is weighted according to the number of moles of each by-product/co-product produced in the global reaction.[5]

In order to yield conservative (higher) estimates of the control costs (cents per kg product) the typical plant capacity chosen for each process was the smallest known to exist. Use of the smallest plant capacity yields a higher estimate of control cost because control equipment capital cost does not decrease in a linear manner as flowrate decreases, due to certain fixed capital costs. Since the estimated flowrates are proportional to plant capacity, capital costs do not decrease in a linear manner as plant capacity decreases. However, plant production is proportional to plant capacity, and control cost is inversely related to plant production. Therefore, control cost increases slightly as plant capacity decreases.

Several processes contain oxygen in the offgas, and the estimated F values were decreased according to the following equation:

$$F \text{ (Corrected)} = F \cdot (1\text{-}4.76 \cdot \text{Volume Percent } O_2 \div \text{Flue-gas to Offgas Ratio})$$

where the flue-gas to offgas ratios are given in Chapter 8, Table 8-3. The oxygen contents for the chemical processes are given in Reference 6.[6] The purpose of this flowrate correction is to decrease the estimated flue-gas flowrate, because of a lower combustion air requirement. As a result, supplementary fuel requirements, heat recovery credits, control equipment sizes, and capital costs will be lower.

The F values of several processes were adjusted further, as a result of rigorous process-specific heat and mass balance calculations, which indicated lower combustion air requirements.[7]

G.7 REFERENCES FOR APPENDIX G

1. Basdekis, H.S. Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry. Control Device Evaluation. Thermal Oxidation Supplement (VOC Containing Halogens or Sulfur). EPA Contract No. 68-02-2577, November 1980. p. III-11.

2. Blackburn, J.W. Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry. Air Oxidation Generic Standard Support. EPA Contract No. 68-02-2577. May 1979. p. III-3.

3. Memo from Galloway, J., EEA, to SOCMI Air Oxidation File. April 17, 1981.

4. Memo from Galloway, J., EEA, to SOCMI Air Oxidation File. February 13, 1981.

5. Ibid.

6. Ibid.

7. Ibid.